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(71) Applicant(s)

NEC Corporation

(Incorporated in Japan)

7-1 Shiba 5-chome, Minato-ku, Tokyo 108-01, Japan

(72) Inventor(s)

Hidemitsu Aoki

Makoto Morita

Mikio Tsuji

(74) Agent and/or Address for Service

Mathys & Squire

100 Grays Inn Road, LONDON, WC1X 8AL,

United Kingdom

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EP 0605882 A1

(58) Field of Search

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KLXC

INT CL⁶ C02F 1/46, H01L

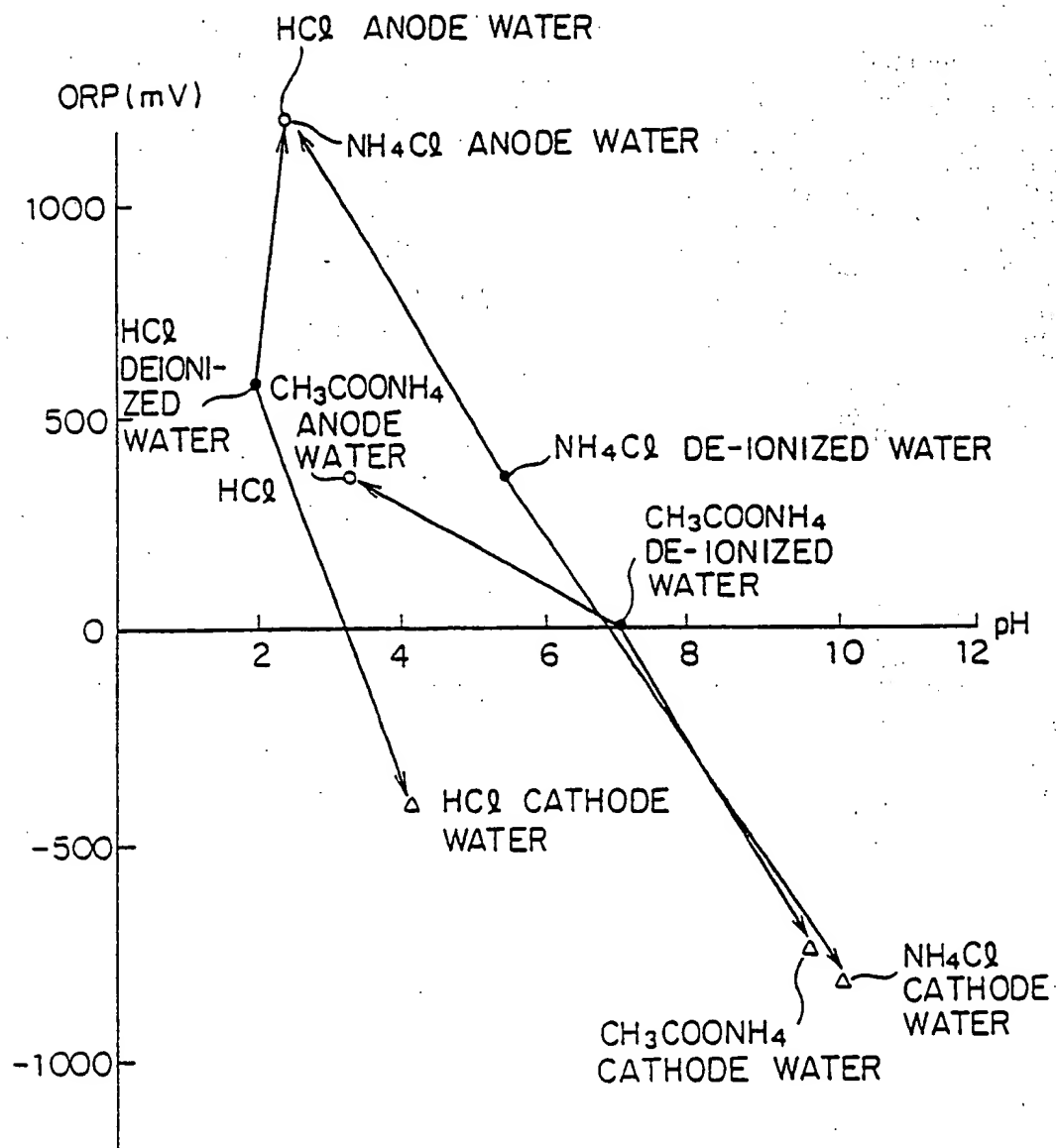
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(54) Wet processing of semiconductor substrates

(57) Electrolyzed waters, including an anode water and a cathode water, having either oxidizing or reducing activity and having either acidity or alkalescency, which is obtained by electrolysis of an aqueous solution prepared by addition of a minute amount of electrolytes, is applied wet processings including cleaning, etching and rinsing processings of semiconductor wafers. The effects of the electrolyzed waters are not lower than those that the conventional acidic or alkalic chemicals provide, and remarkably reduces quantity of chemicals used in wet processings in semiconductor manufacturing. The electrolytes are selected from ammonium salts, hydrochloric acid and aqueous ammonia. Further chemicals may be added to the electrolytic water and various gases may be bubbled through the water.

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FIG. 1



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FIG. 2

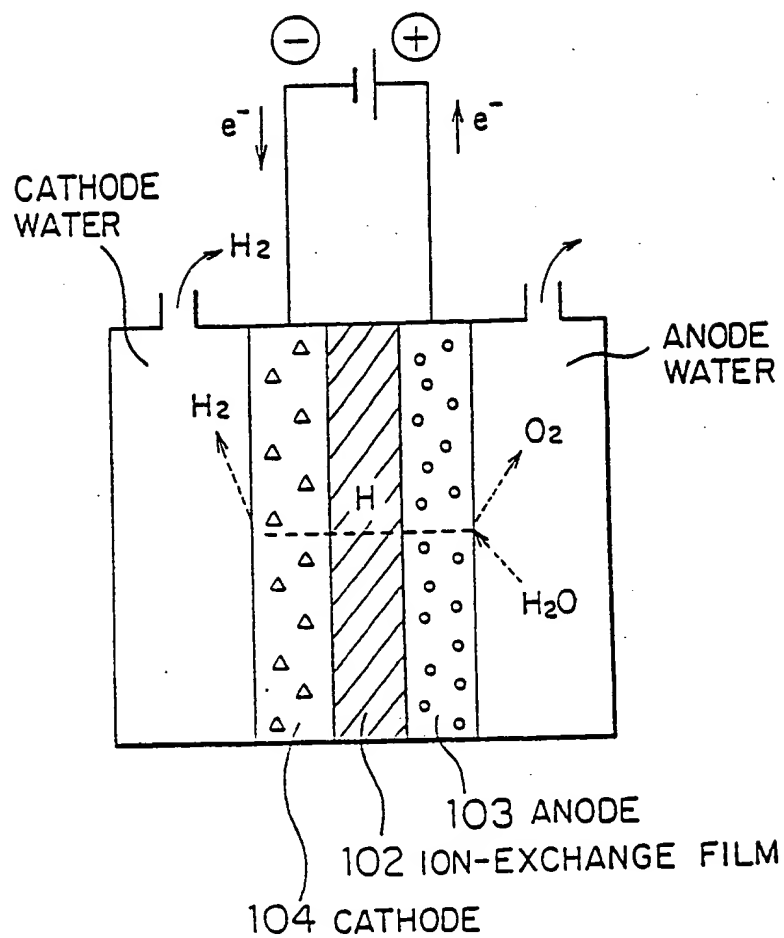
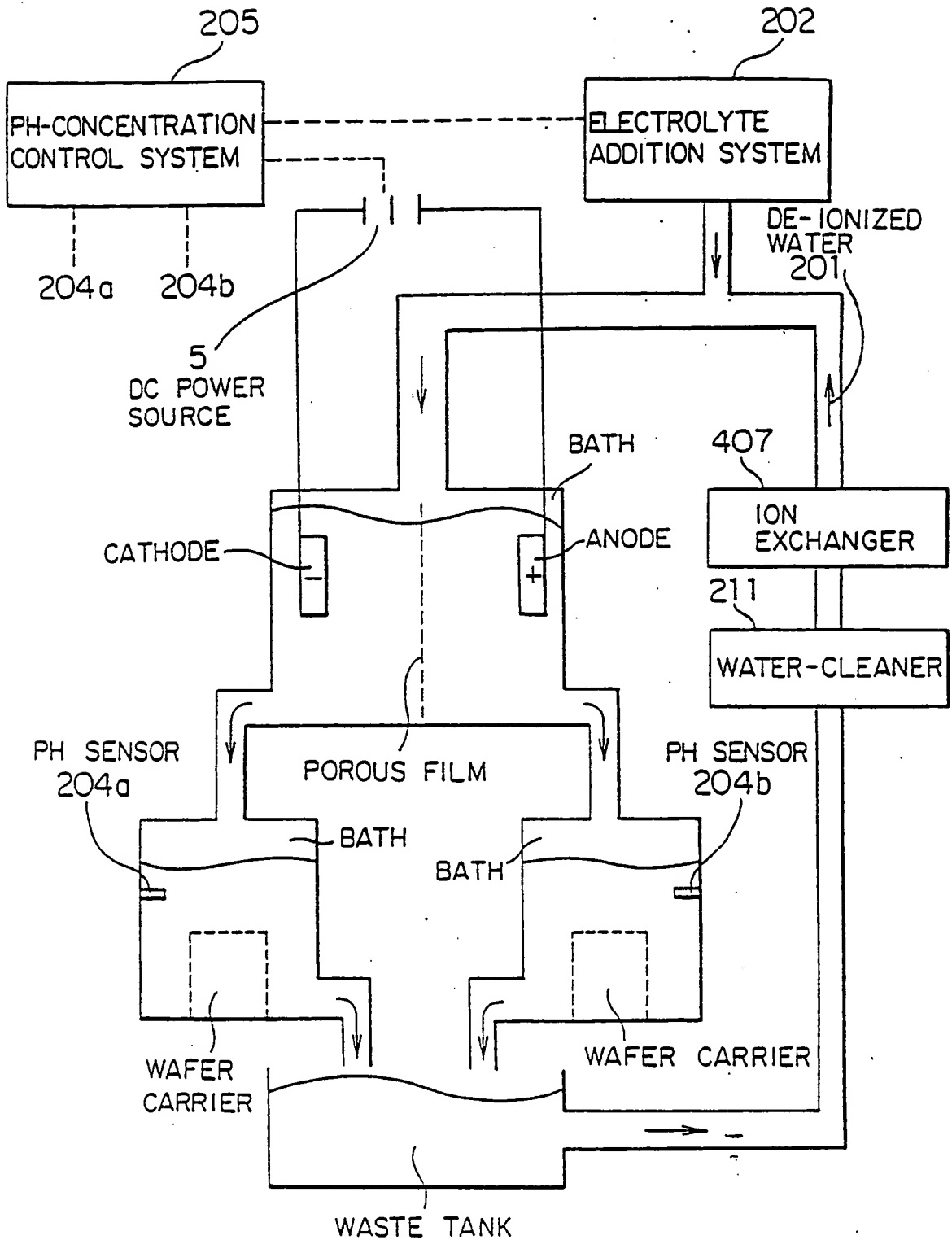
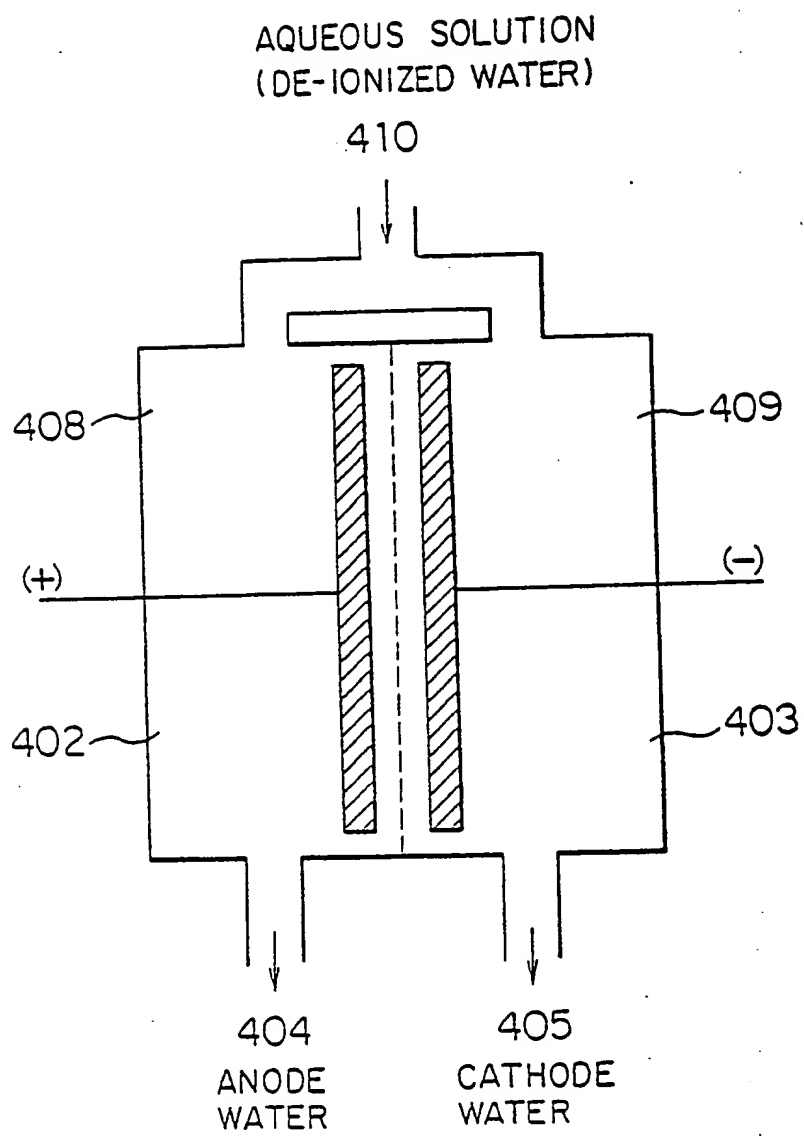


FIG. 3



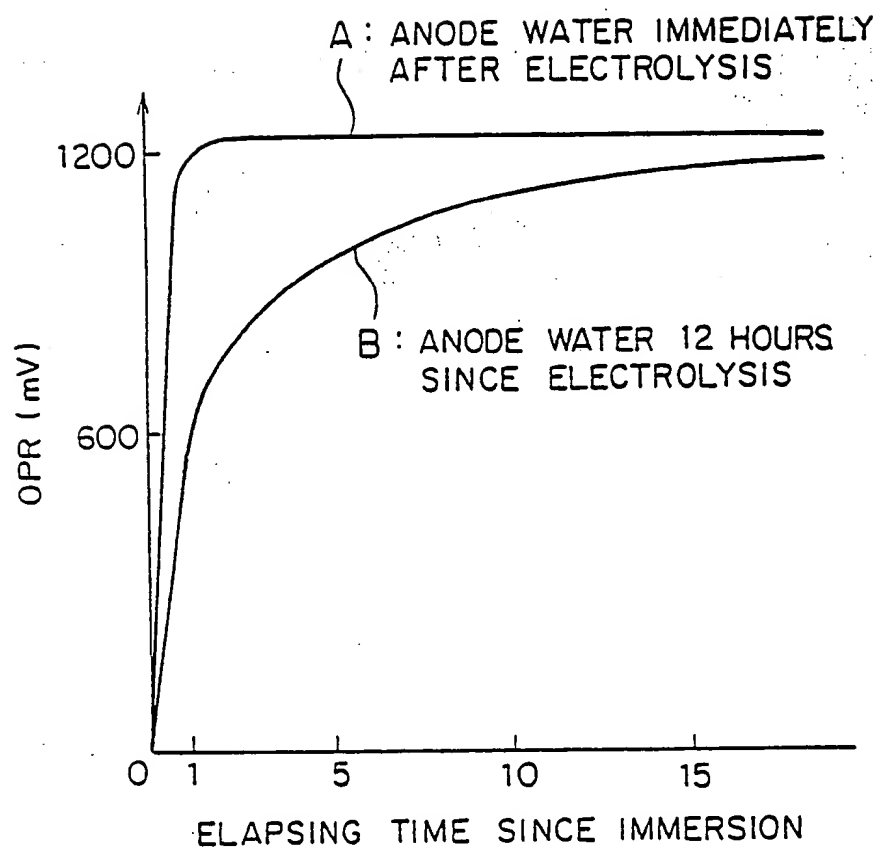
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FIG. 4



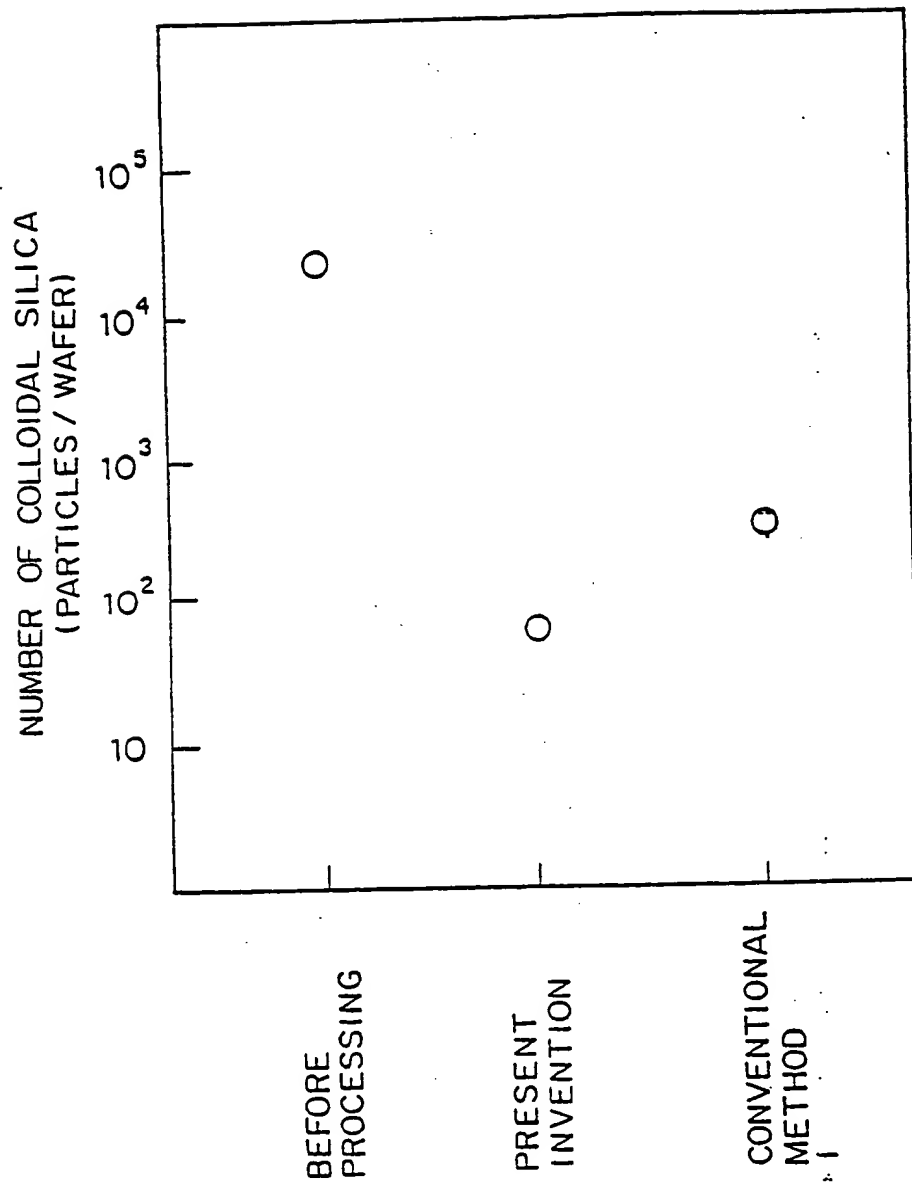
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FIG. 5



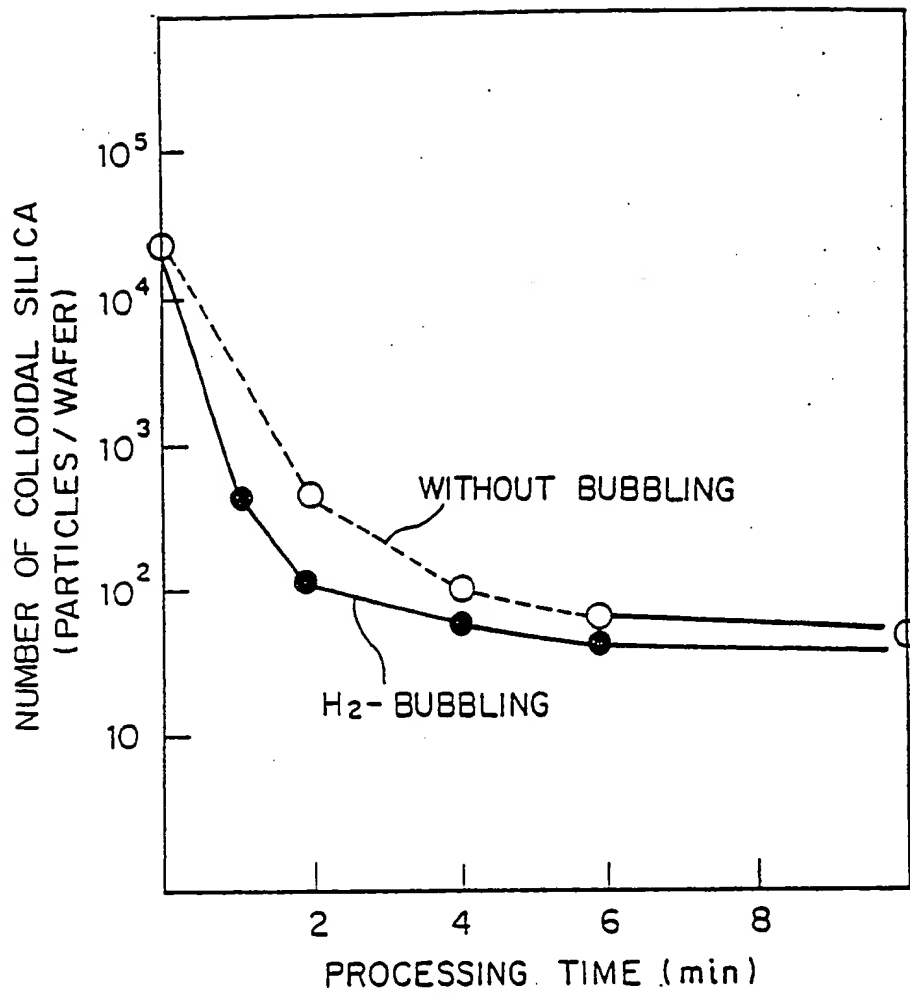
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FIG. 6



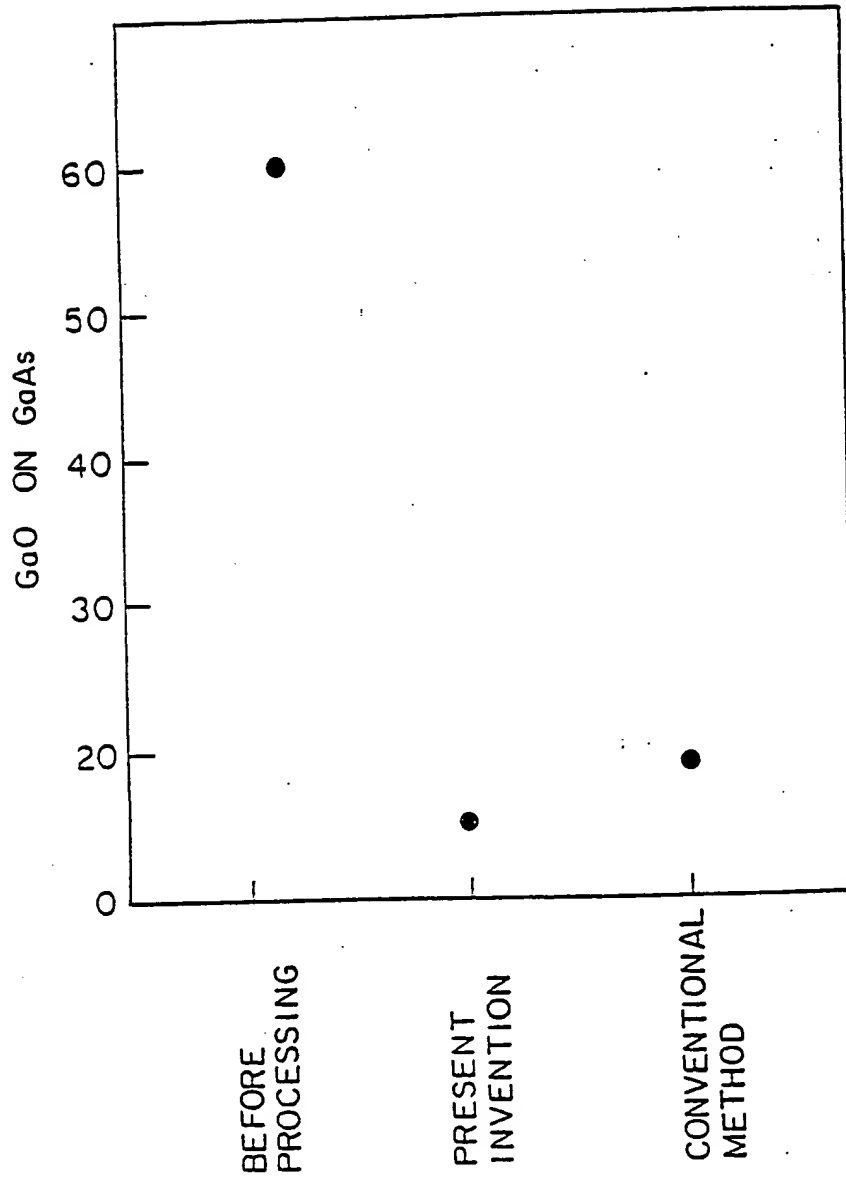
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FIG. 7



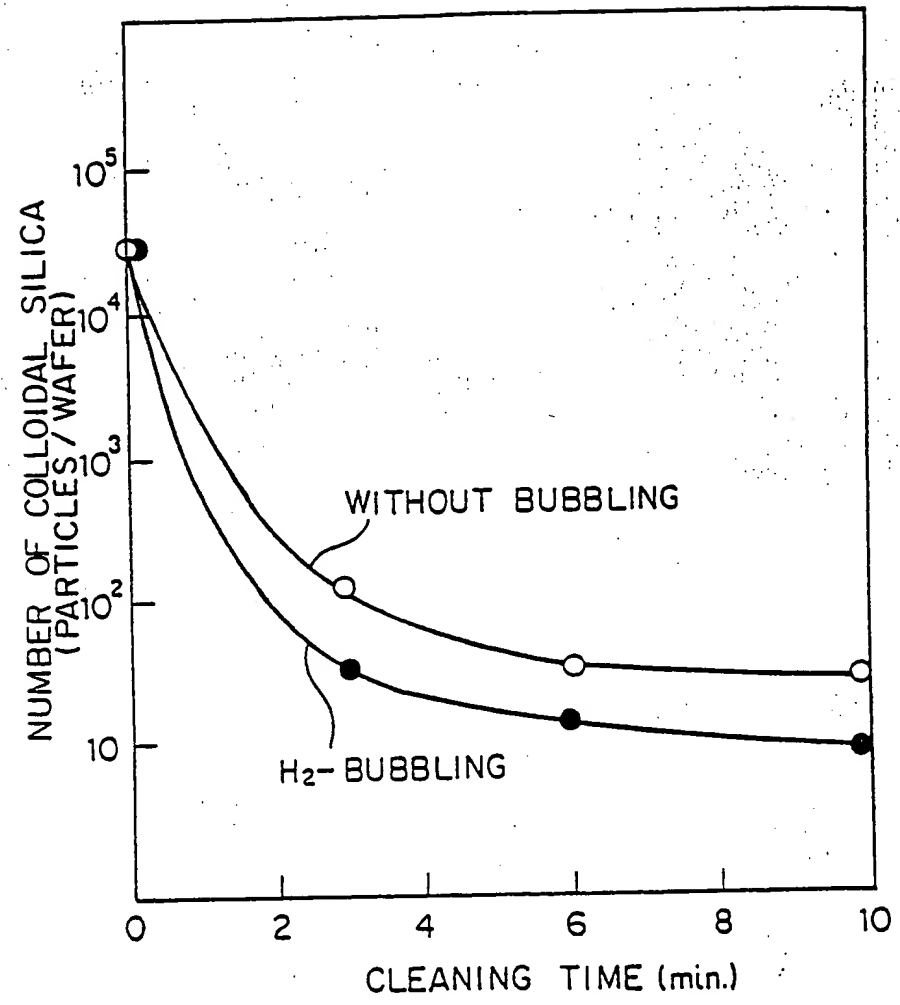
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FIG. 8



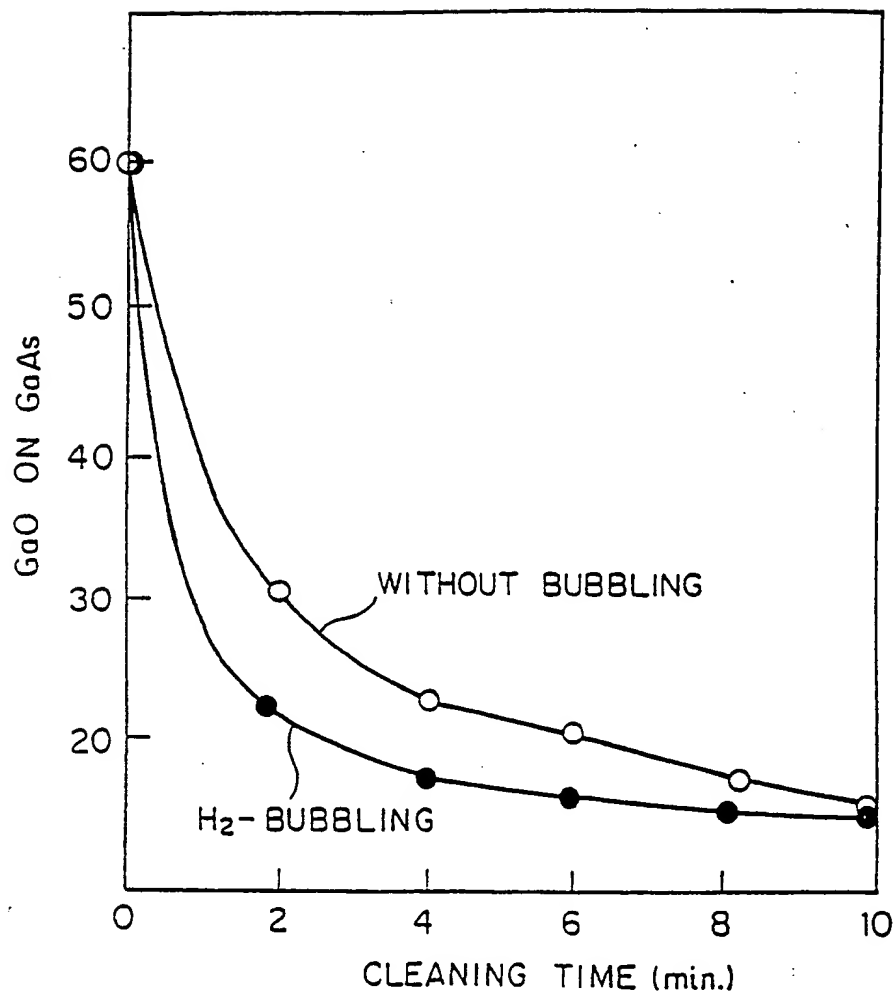
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FIG. 9



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FIG. 10



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FIG. 11

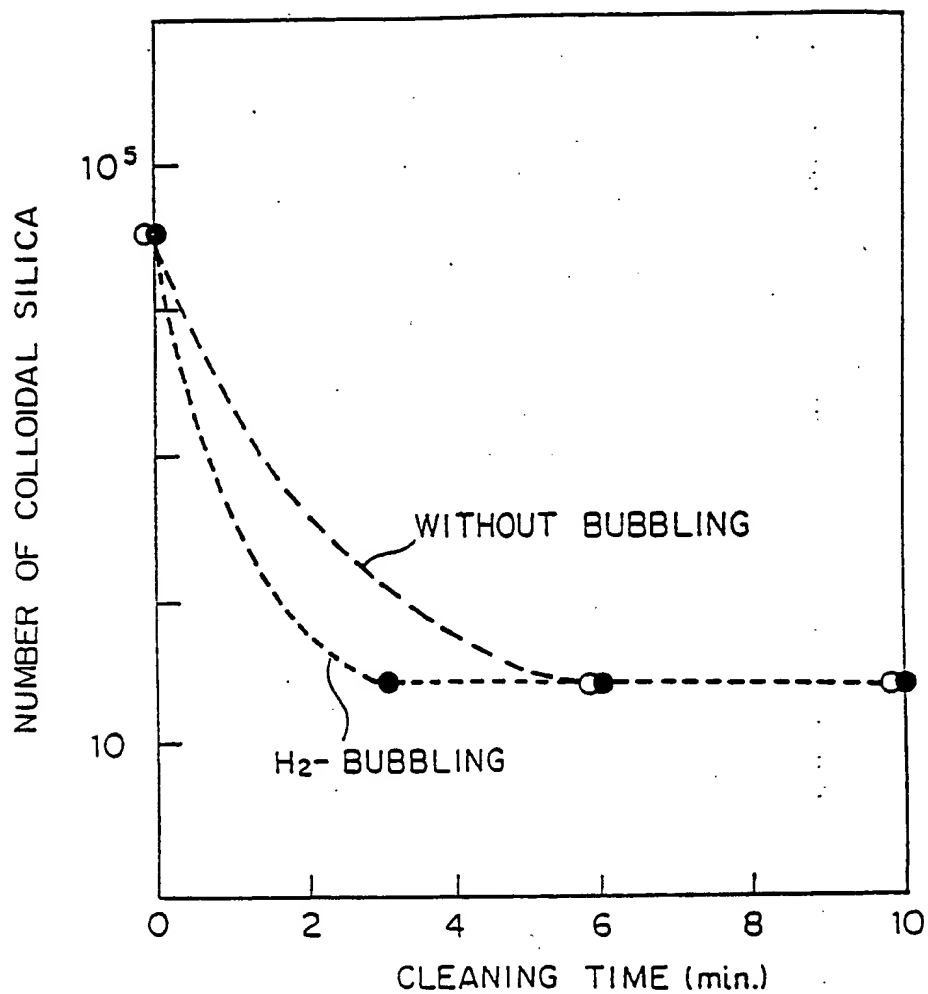


FIG. 12A

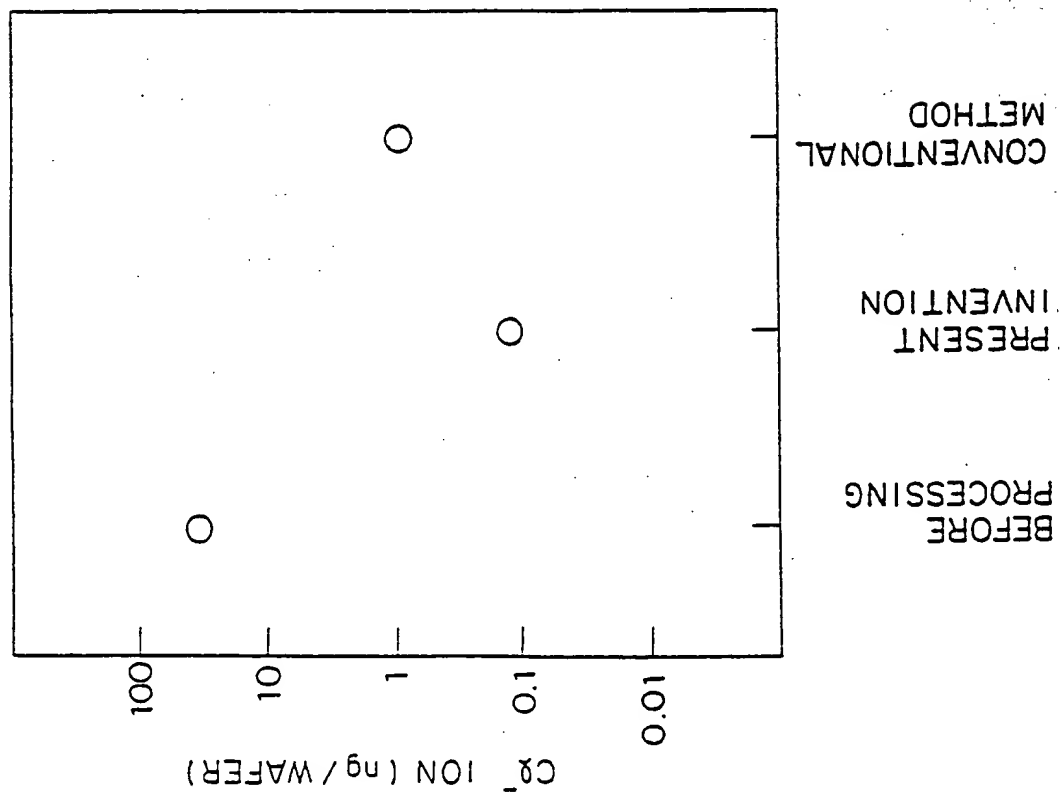
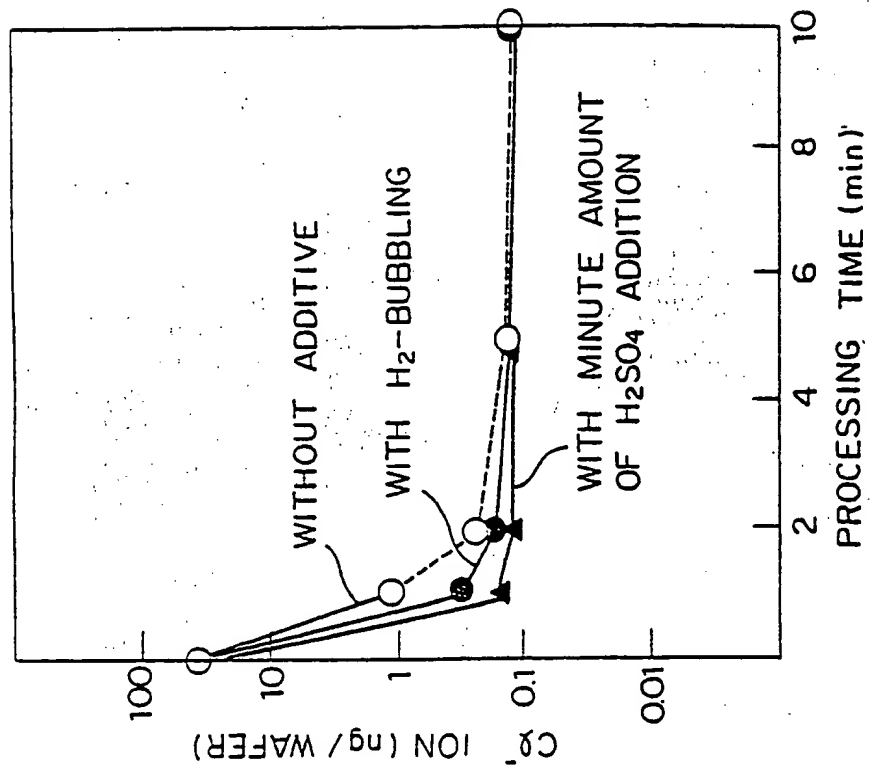
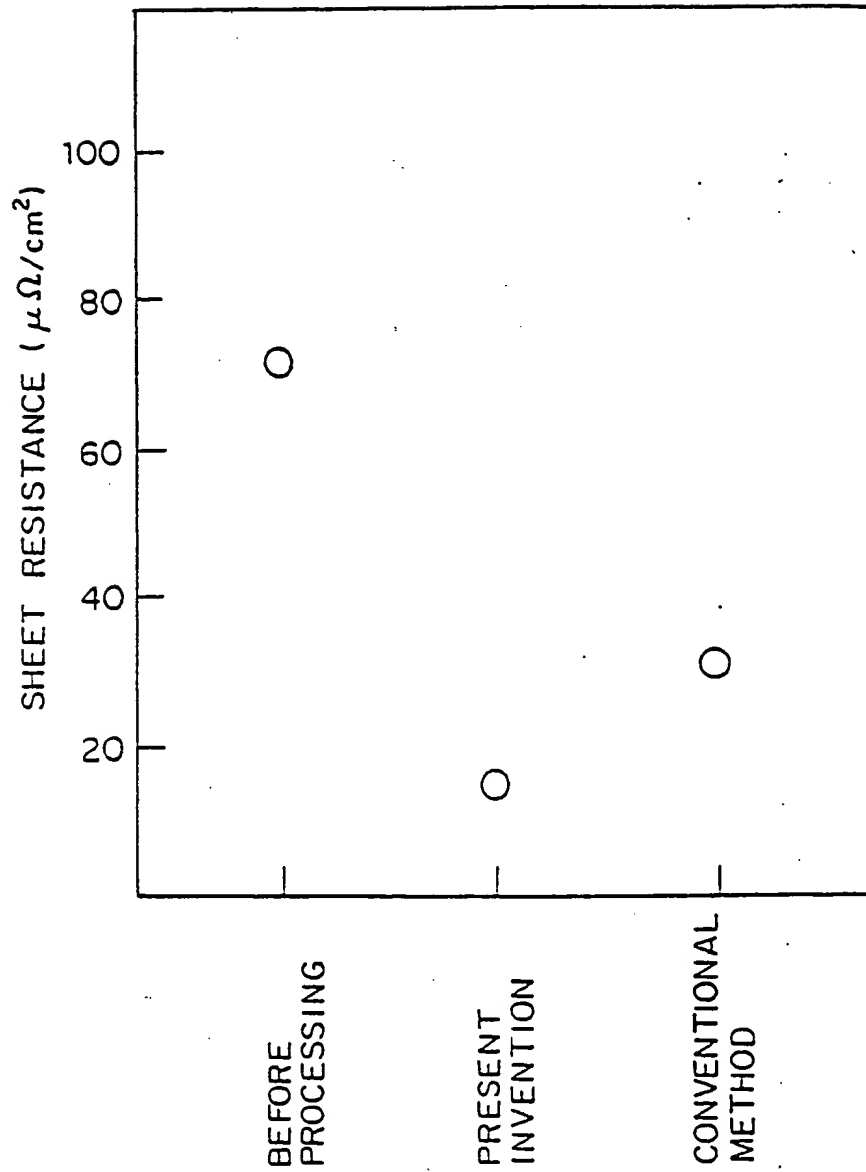


FIG. 12B



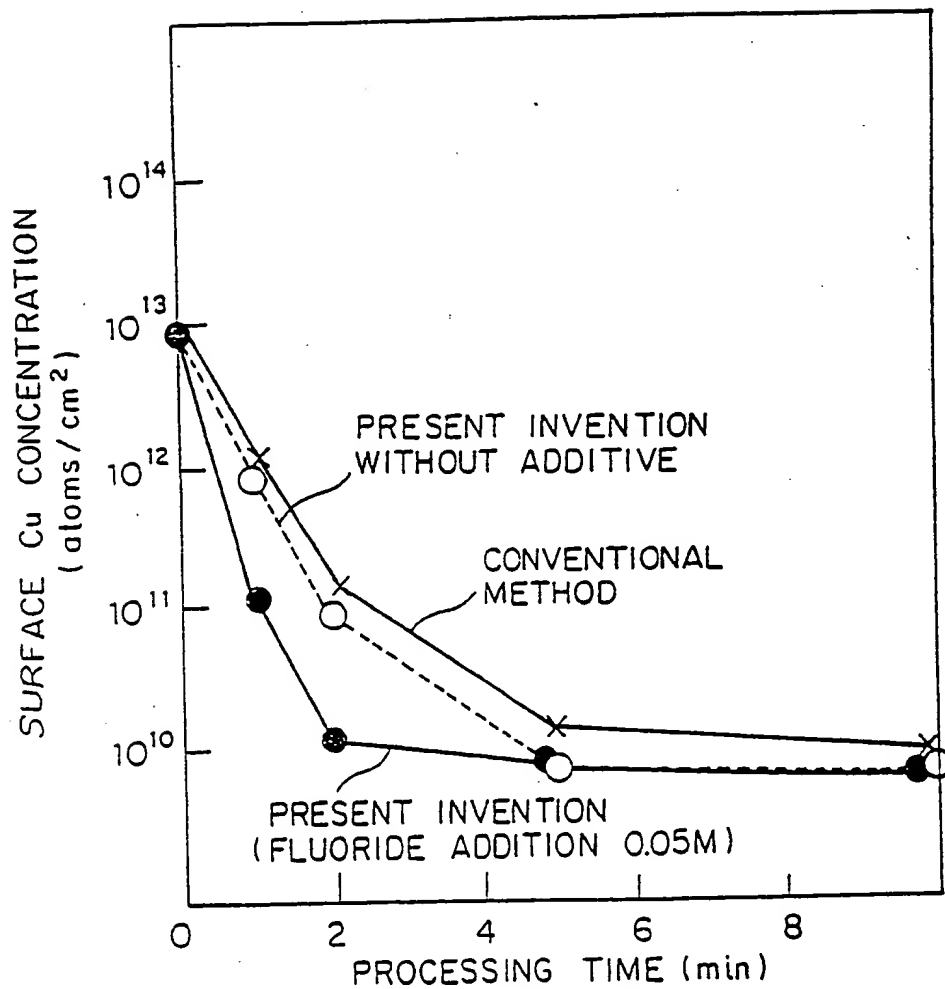
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FIG. 13



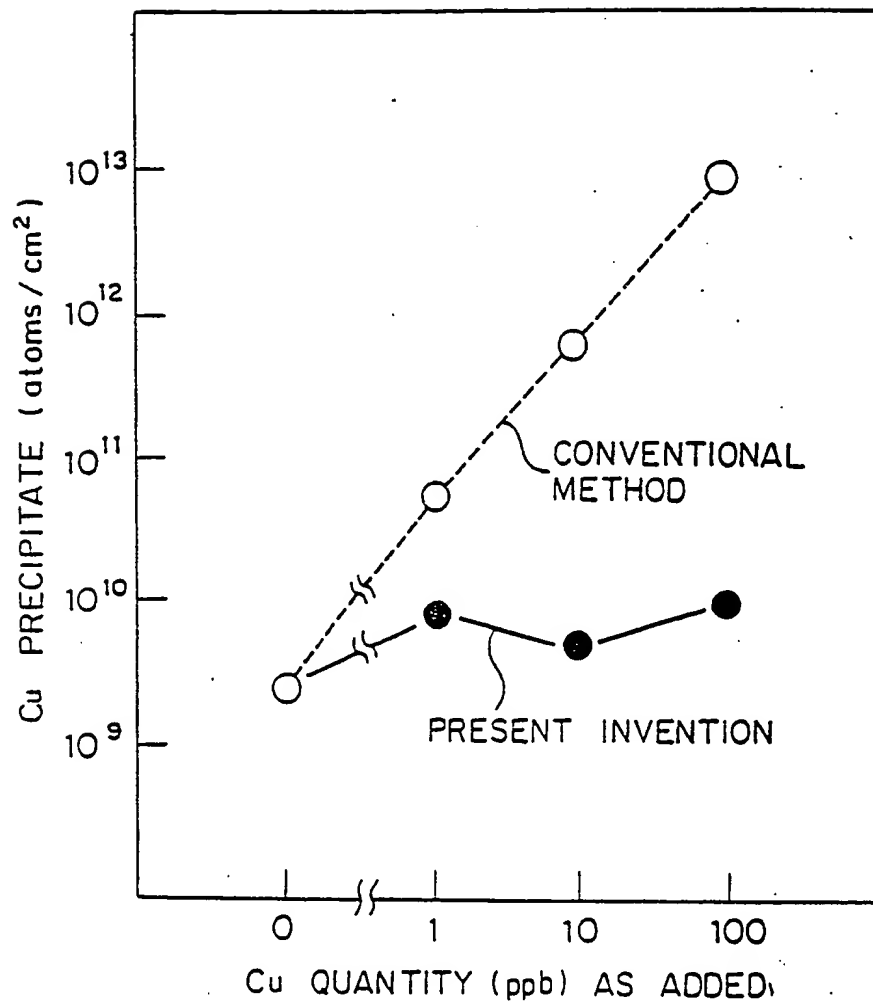
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FIG. 14



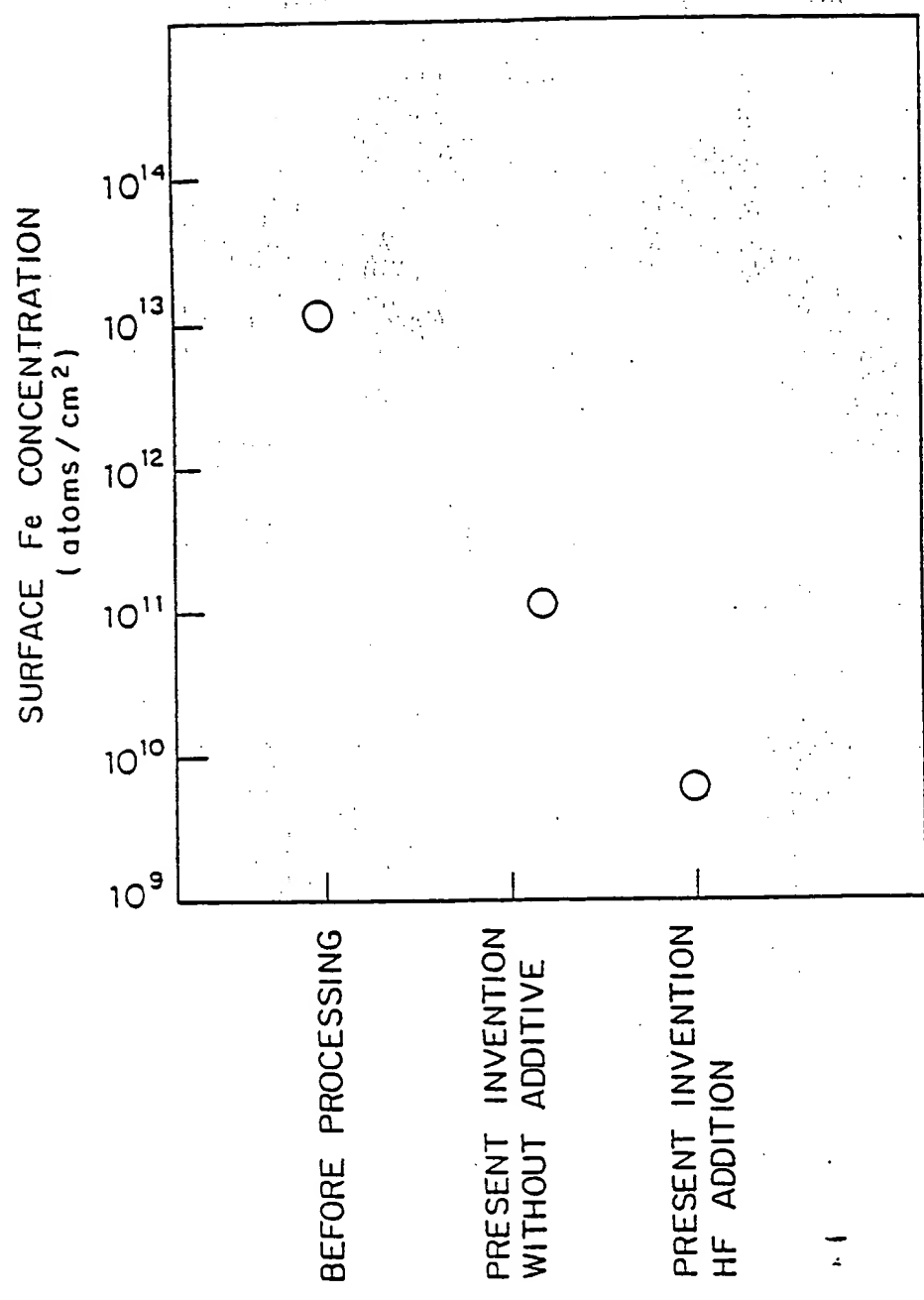
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FIG. 15



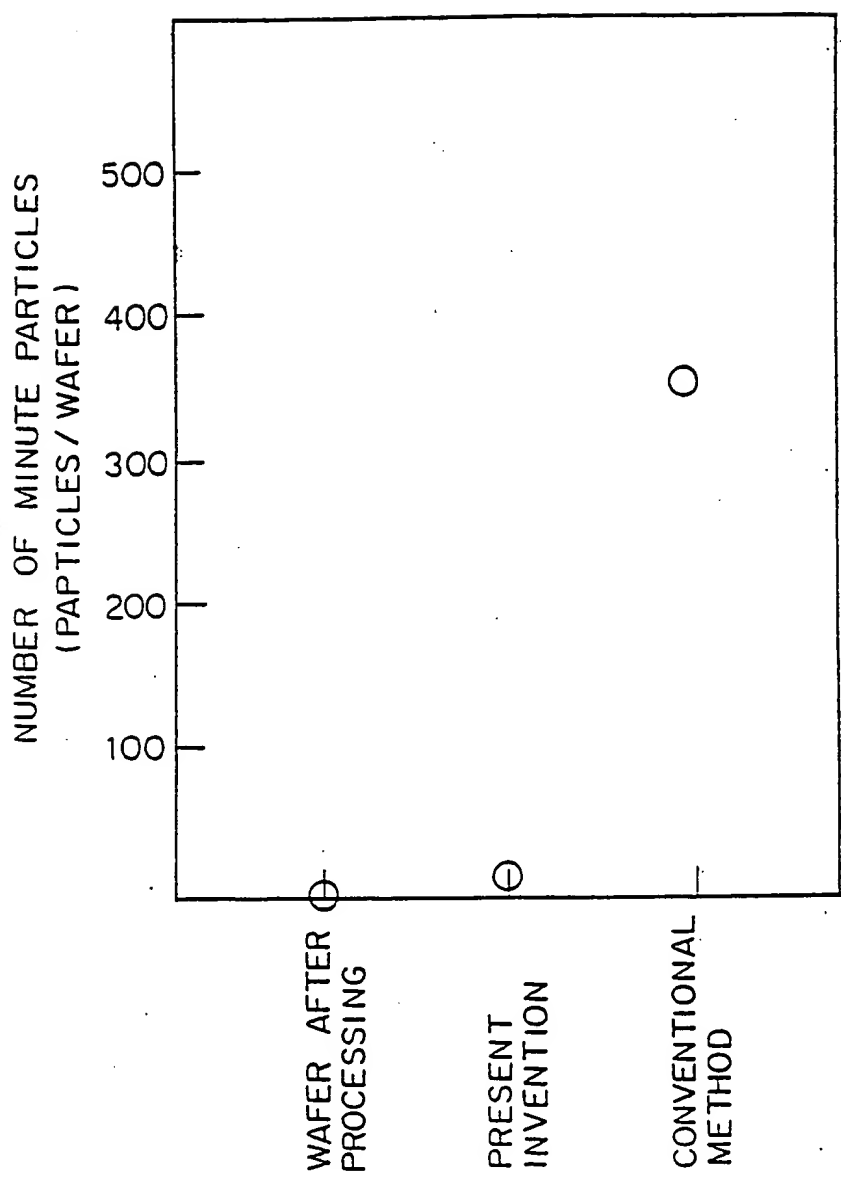
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FIG. 16



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FIG. 17



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FIG. 18

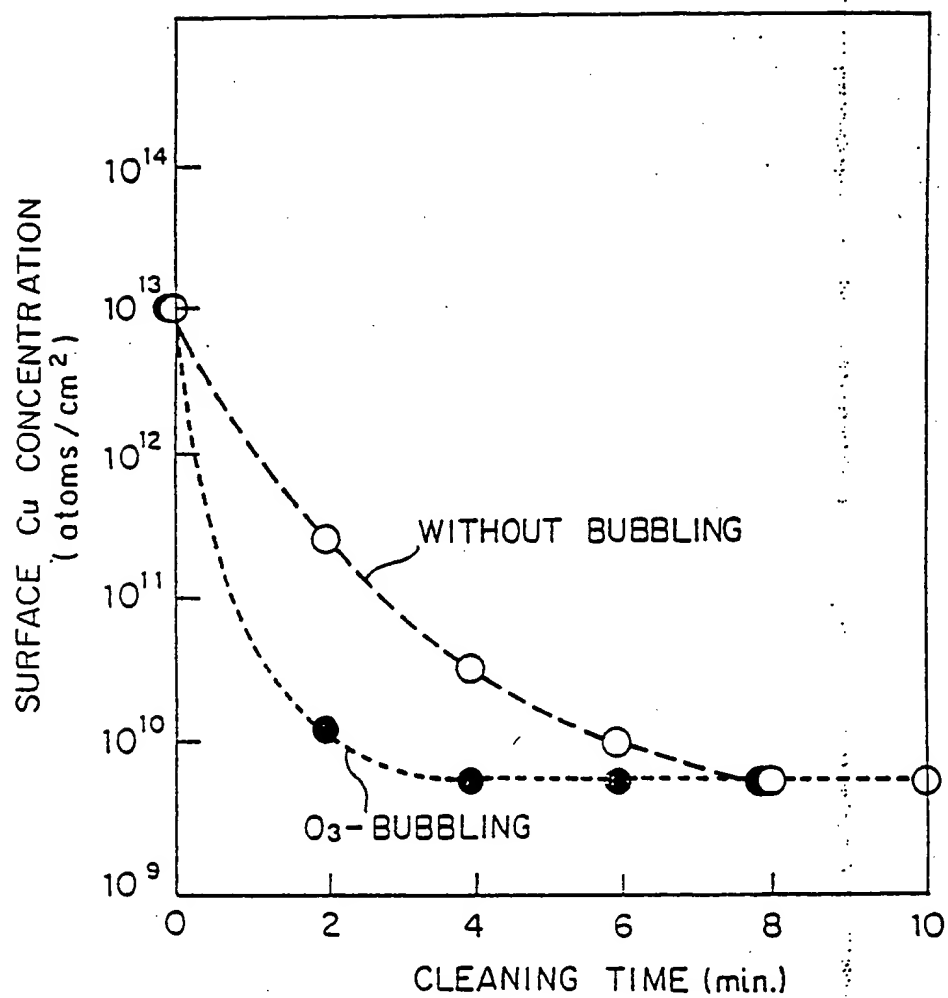


FIG. 19A

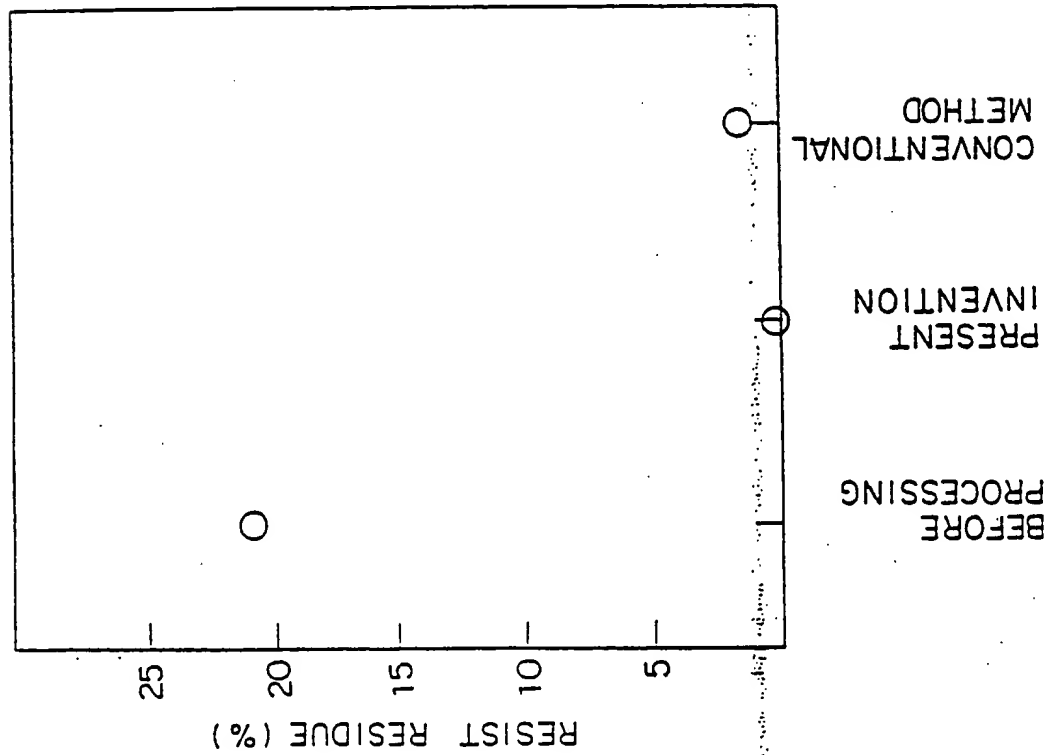
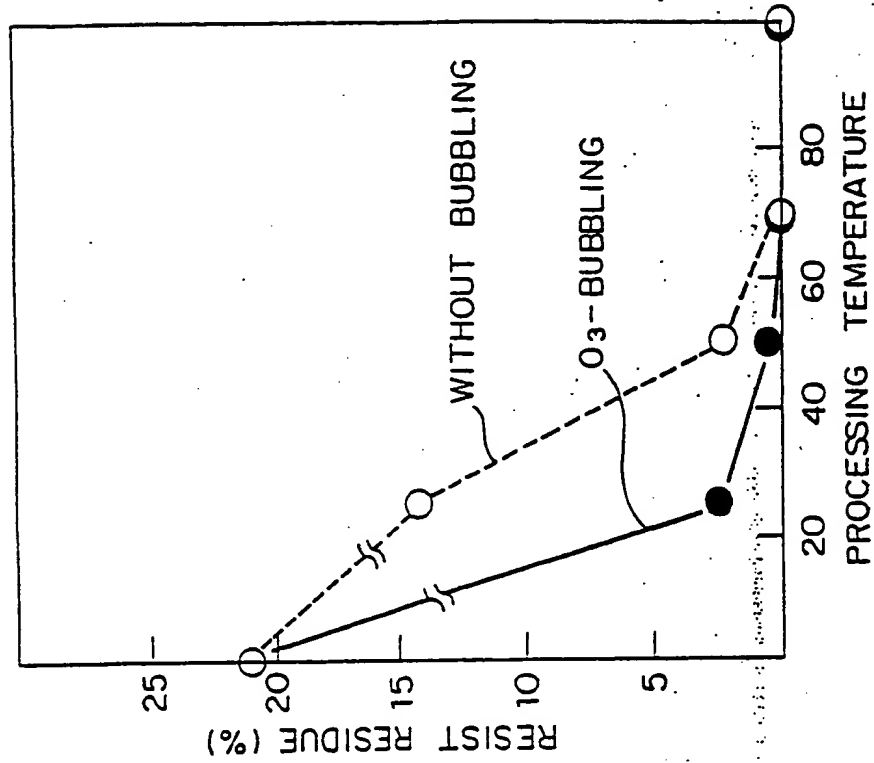


FIG. 19B



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FIG. 20

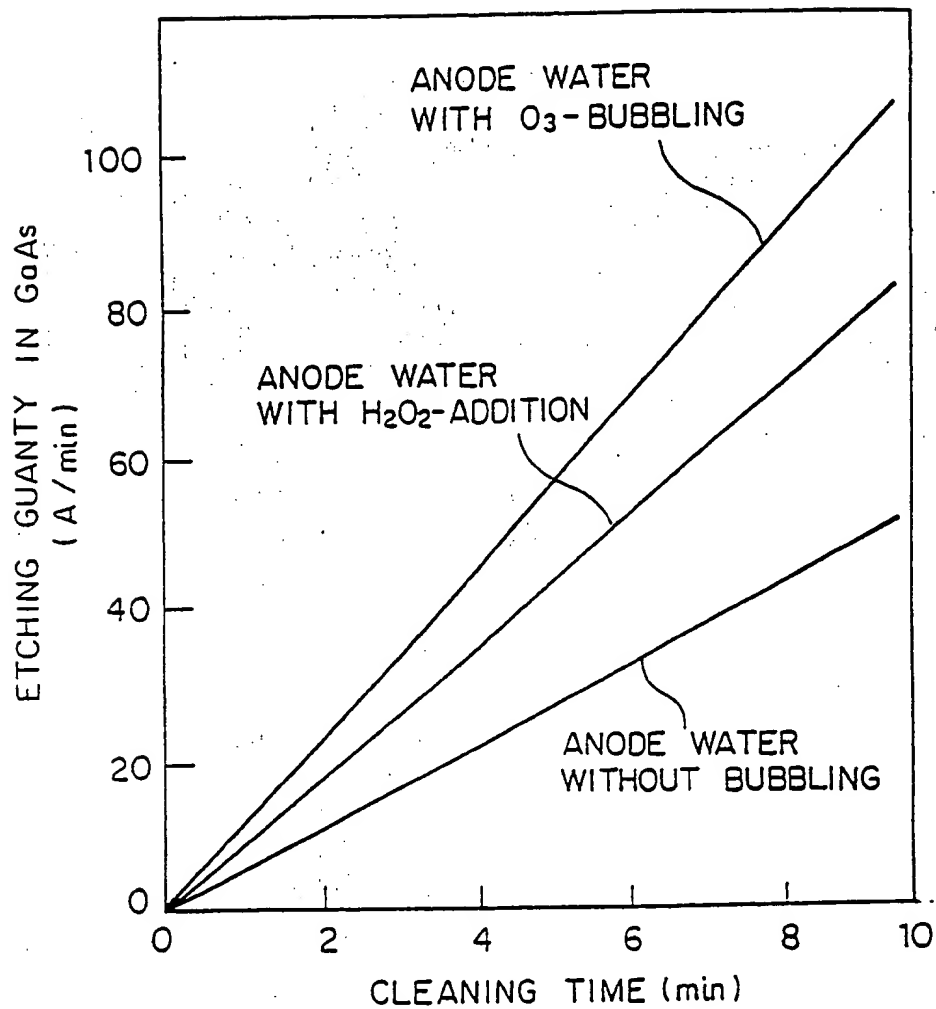


FIG. 21A

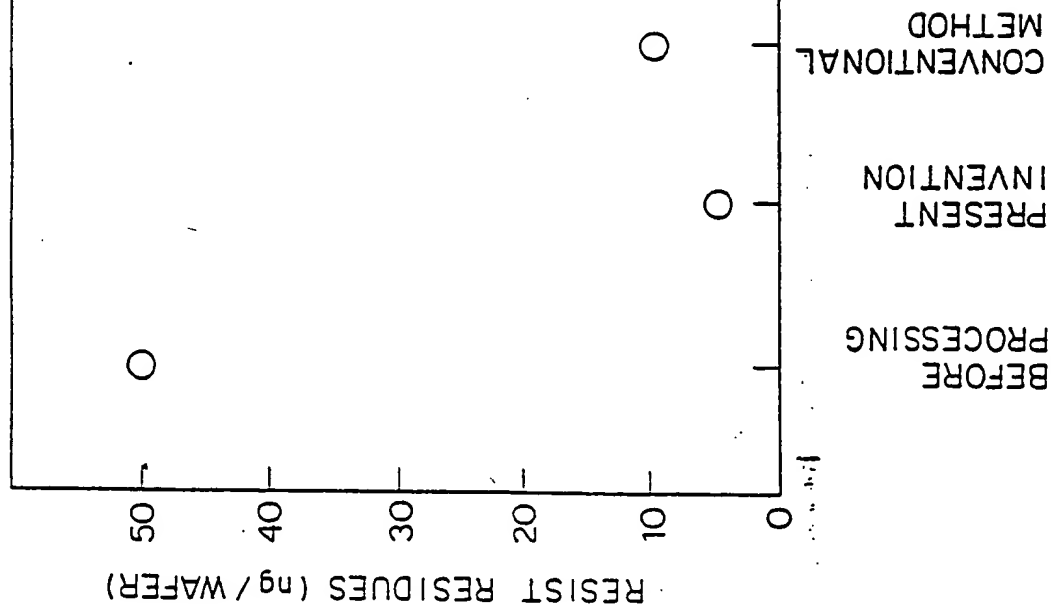
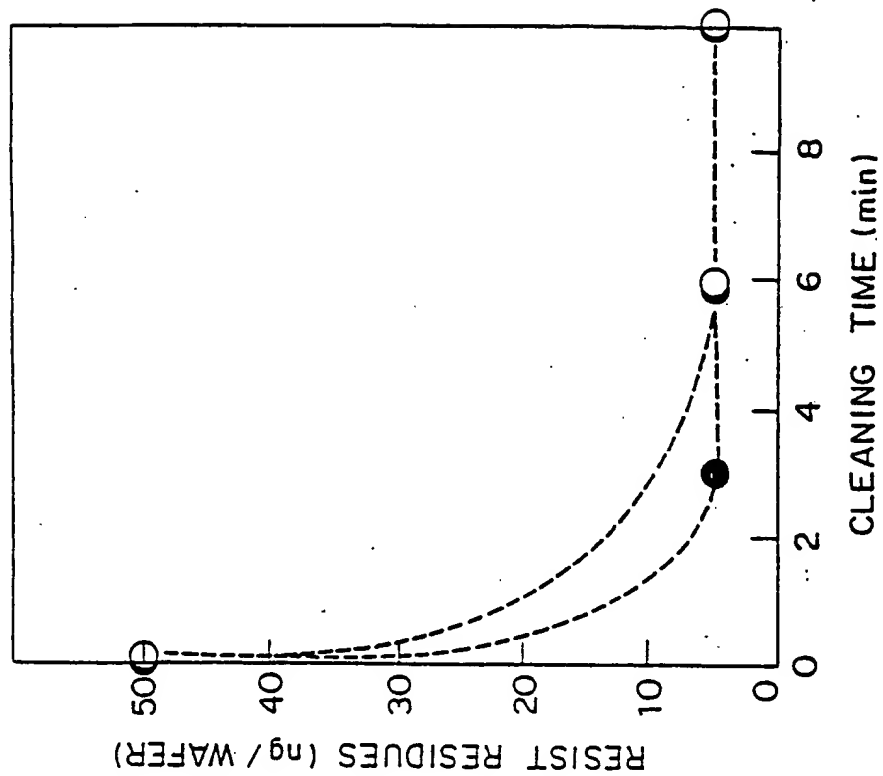


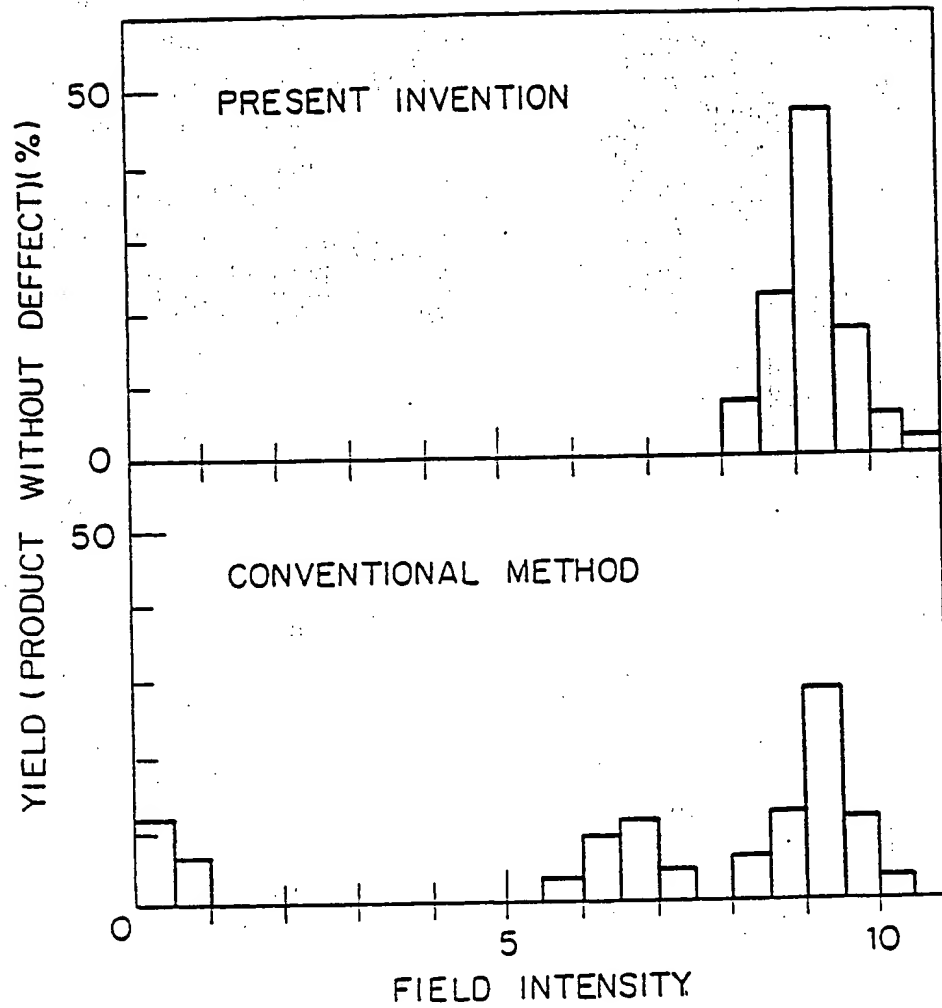
FIG. 21B



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FIG. 22



METHOD FOR WET PROCESSING OF
A SEMICONDUCTOR SUBSTRATE

BACKGROUND OF THE INVENTION

(a) Field of the Invention

The present invention relates to a method for wet processing of a semiconductor substrate and, more particularly, to a new method for wet processing of a semiconductor substrate capable of reducing the amount of chemicals used in cleaning, etching or rinsing steps in manufacturing semiconductor devices.

(b) Description of the Related Art

10 The semiconductor industry that supports today's information-based society has a serious problem, namely to reduce the large quantities of chemicals which are consumed in the manufacturing processes for semiconductor devices. The volume reduction in consumed chemicals is urgent not only from the pollution problem point of view but also from the treatment fee reduction point of view for waste chemicals, taking the scale and the promising future of the electronics industry into consideration, although they do not consume as much chemicals as so-called heavy industries do. The present

20

invention is directed to contributing to volume reduction in chemicals wasted in so-called wet processings for manufacturing semiconductor devices such as cleaning, etching or rinsing process.

5 There exist many so-called wet processing steps for manufacturing semiconductor devices, such as cleaning, etching and rinsing. Even if confined to steps conducted by semiconductor substrate manufacturers after a step for pulling-up single crystals, the wet processes extend to
10 cleaning processes conducted between slicing, mechanical lapping and chemically mechanical polishing steps by employing organic chemicals, a cleaning process for removing sludges generated in the mechanical lapping step, etching processes employing strong acids and alkalis, and chemically
15 mechanical polishing process itself which consumes vast volume of chemicals.

 Furthermore, after the wafers are shipped to semiconductor device manufacturers, the wet processes begin with, in general, so called Dr. Branson or RCA Cleaning
20 conducted for wafer surfaces before starting manufacturing steps and then extend to photoresist processes in the multiple photo-engraving steps and to acid or alkali etching processes employing vast volume of chemicals in steps for selectively etching oxide or metallic films.

25 The many species of wet processes for cleaning, etching

and rinsing the semiconductor wafers mentioned above are classified into a process for etch-removing the semiconductor surfaces, a process for removing metallic contaminants, organic particles, photoresist residues and ionic residuals adhered onto the surface substantially without etching off any underlying semiconductors, metals and insulators, and a process for etch-removing natural oxide films and organic films adhered onto the underlying semiconductors, metallic and organic films etc.

Some of wet processings which have been used are tabulated on Table. 1.

Table. 1

15	Treatment	Chemicals (Composition)	Effect/Etch Rate
20	Etch		
	Si	Alkali Solu. (KOH, Choline)	40-100 A/min
	Si	APM ($\text{NH}_4\text{OH}:\text{H}_2\text{O}_2:\text{H}_2\text{O}=1:4:20$)	2-10 A/min
	Compound	SPM ($\text{H}_2\text{SO}_4:\text{H}_2\text{O}=5:1$)	50-1000 A/min
	Metal	dil. HCl aq.	0.1-1.0 $\mu\text{m}/\text{min}$
25	Insulator(SiO_2)	DHF ($\text{HF}:\text{H}_2\text{O}=1:50-400$)	10-500 A/min
	Remove on Si		
	Metal	SPM ($\text{H}_2\text{SO}_4:\text{H}_2\text{O}=5:1$)	$<10^{10}$ atom/ cm^2

Metal	HPM ($\text{HCl}:\text{H}_2\text{O}_2:\text{H}_2\text{O}=1:1:6$)	<10 ¹⁰ atom/cm ²
Organic	APM ($\text{NH}_4\text{OH}:\text{H}_2\text{O}_2:\text{H}_2\text{O}=1:4:20$)	<100 pcs/wafer
Organic	SPM ($\text{H}_2\text{SO}_4:\text{H}_2\text{O}=5:1$)	<100 pcs/wafer
Inorganic Part.	APM ($\text{NH}_4\text{OH}:\text{H}_2\text{O}_2:\text{H}_2\text{O}=1:4:20$)	<100 pcs/wafer
Remove		
Metal Contami.	HPM ($\text{HCl}:\text{H}_2\text{O}_2:\text{H}_2\text{O}=1:1:6$)	<10 ¹⁰ atom/cm ²
Org./Inorganics	APM ($\text{NH}_4\text{OH}:\text{H}_2\text{O}_2:\text{H}_2\text{O}=1:4:20$)	<100 pcs/wafer
Remove		
Metal	SPM ($\text{H}_2\text{SO}_4:\text{H}_2\text{O}=5:1$)	<10 ¹⁰ atom/cm ²
Metal	HPM ($\text{HCl}:\text{H}_2\text{O}_2:\text{H}_2\text{O}=1:1:6$)	<10 ¹⁰ atom/cm ²
Metal	HNO_3	<10 ¹⁰ atom/cm ²
Organics	APM ($\text{NH}_4\text{OH}:\text{H}_2\text{O}_2:\text{H}_2\text{O}=1:4:20$)	<100 pcs/wafer
Organics	SPM ($\text{H}_2\text{SO}_4:\text{H}_2\text{O}=5:1$)	<100 pcs/wafer
Inorganics	APM ($\text{NH}_4\text{OH}:\text{H}_2\text{O}_2:\text{H}_2\text{O}=1:4:20$)	<100 pcs/wafer
Remove Natural Oxide Film On Si	DHF ($\text{HF}:\text{H}_2\text{O}=1:50-400$)	

It is described in "A Cleaning Method Utilizing Red/Ox
Procedures - A New Cleaning Method in Electronics Industry "
written by Sumita et al. on "The Journal for Cleaning

Design" published by Kindai Hensyu-sha, Spring Issue of 1987 (referred to as "Ref. 1" hereinafter) that electrolyzed water has special activities. A step for electrolyzing water is illustrated in a schematic view of Ref. 1 (Fig. 2) wherein two electrodes 103 and 104 are installed in a water bath 101 and separated from each other by ion-exchange film 102. An electrolyzing reaction is effected by applying a DC voltage between two electrodes, with electrode 103 being an anode and electrode 104 being a cathode. It is recited that the water formed on the anode side (referred to as "an anode water" hereinafter) exhibits acidic because of increase in H^+ ions while the water formed on the cathode side (referred to as "a cathode water" hereinafter) exhibits alkalic because of an increase in OH^- ions.

Various conditions and situations are investigated to apply the electrolyzed waters to wet processing steps in manufacturing semiconductor devices. According to Ref. 1, it is reported that two species of waters which generate in anode and cathode chambers, respectively, by electrolysis of de-ionized water have special activities including cleaning effects beside different oxidation/reduction potentials (referred to as "ORP" hereinafter) and different pH values which indicate extents of being acidic and alkalic from ordinal de-ionized water. Accordingly, cleaning, etching and rinsing effects of the waters, which are prepared in the

cathode and anode chambers by the method according to Ref.

1. are re-examined for application to steps in manufacturing semiconductor devices.

Unfortunately, the specific effects which are peculiar
5 to the waters according to Ref. 1 are, however, not re-
confirmed in our experiments, although there is a little
suspicion that the method according to Ref. 1 is not
strictly traced to in our experiments. Then, the
electrolyzed waters provided by tracing the method according
10 to Ref. 1 are directed to application to steps in
manufacturing semiconductor devices on a condition that a
minute amount of chemicals is added to the de-ionized water,
making a compromise with the initial principle that any
amount of chemicals should not be utilized during wet
15 processing. Ref. 1 does recite electrolyzing electrolytic
solutions but does not recite any concrete species of the
electrolytes.

We have disclosed methods applied to steps for
manufacturing semiconductor devices in JP Patent Application
20 No. 5(1993)-105991. In JP Patent Application No. 5(1993)-
105991, an apparatus for forming electrolyzed water
illustrated in Fig. 3 of the present application has been
proposed, wherein it is demonstrated in embodiments that
addition of a minute amount of quaternary alkyl ammonium
25 combined with cations except for halogen ions into de-

ionized water 201 is useful for electrolyzing of water. Addition of the specified chemicals verified that the electrolyzed water is applicable to wet processing steps in manufacturing semiconductor devices. The apparatus shown in Fig. 3 enables a precise pH control because pH control system 205 controls pH through feedback of pH values measured by sensors 204a and 204b for generated anode and cathode waters, to an electrolyte addition quantity control system 205.

Those methods as described above have effects on some limited parts of semiconductor wet processings. However, it is found that application to more universal processings (not only to cleaning but also to etching and rinsing processings) requires considerations about conditions of electrolyzed waters and of cleaning procedures necessary for respective processes, especially about the ORP value which is an indicator of oxidizing/reduction ability of water, about resolved quantities of O_3 and H_2 gases and about oxoacid quantity of halogen. It requests trials for enabling reduction in chemicals consumed in all semiconductor processings and a cost reduction in treatment of waste liquids. Namely, the subject to reduce an environmental load in semiconductor processings is an urgent problem that should be solved immediately.

SUMMARY OF THE INVENTION

In view of foregoing, it is an object to provide a new method for wet processing of semiconductor substrate capable of reducing chemicals consumed in the processing.

5 The present invention is directed to a method for processing a semiconductor wafer including steps of: adding at least one of electrolyte selected from a group consisting of ammonium chloride, ammonium acetate, ammonium fluoride, ammonium nitrate, ammonium bromide, ammonium iodide,
10 ammonium sulfate, ammonium oxalate, ammonium carbonate, ammonium citrate, ammonium formate, hydrochloric acid and aqueous ammonia at a rate ranging from 8×10^{-2} to 2×10^{-5} mol/l into de-ionized water to prepare an aqueous solution; electrolyzing the aqueous solution to prepare at least one
15 of an anode and a cathode water. At least a region of a semiconductor wafer to be processed may be dipped into an aqueous solution (referred to as

a processing solution) including at least one of the anode and cathode waters or the processing solution may otherwise be
20 applied to the region to be processed.

 The present invention is further directed to a method for processing a surface of a semiconductor wafer in a processing solution prepared by addition of at least one acid selected from a group consisting of chelating agents,
25 hydrochloric acid, formic acid and nitric acid, into an

anode water which is prepared by electrolyzing water, at a rate ranging from 10^{-2} to 10^{-4} mol/l. Thus, the method may involve: adding at least one electrolyte selected from a group consisting of the electrolytes as recited above into water at a concentration ranging from 8×10^{-2} to 2×10^{-5} mol/l to prepare an aqueous solution; electrolyzing the aqueous solution to prepare an anode water; adding at least one acid selected from a group consisting of chelating agents, hydrochloric acid, formic acid and nitric acid into the anode solution at a molar concentration of the acid ranging from 10^{-2} to 10^{-4} to prepare a processing solution; and dipping a region to be processed of a semiconductor wafer into the processing solution or otherwise applying the processing solution to the region to be processed.

Moreover, the present invention is directed to a method for processing a semiconductor wafer including steps of: adding at least one electrolyte selected from a group consisting of the electrolytes as recited above into water at a concentration ranging from 8×10^{-2} to 2×10^{-5} mol/l to prepare an aqueous solution; electrolyzing the aqueous solution to prepare an anode water; adding at least one of chemical species consisting of hydrofluoric acid and ammonium fluoride at a rate providing a molar concentration ranging from 1/10 to 1/500 of the molar concentration of the electrolyte into the anode water to obtain a processing

solution: dipping a region to be processed of a semiconductor wafer into the processing solution or pouring the processing solution onto the region to be processed.

Furthermore, the present invention is directed to a method for processing a semiconductor wafer including a step of: dipping a region to be processed of the semiconductor wafer into one of processing solutions including a first processing solution obtained by adding H_2O_2 into a cathode water, which is prepared by addition of at least one electrolyte selected from the group consisting of the electrolytes as recited above at a concentration ranging from 8×10^{-2} to 2×10^{-5} mol/l. at a quantity ranging between a value substantially same as the quantity of the electrolyte as added and a tenth thereof, a second processing solution containing oxoacid ions of chlorine, bromine or iodine at a concentration more than 10^{-3} mol/l. a third processing solution prepared by bubbling the anode water as recited above with Cl_2 , Br_2 and I_2 gases or O_3 gas or otherwise applying one of the processing solutions to the region to be processed of the semiconductor wafer.

Furthermore, the present invention is directed to a method for processing a semiconductor wafer including dipping a region to be processed of the wafer into a processing solution prepared by bubbling the cathode water as recited above with H_2 gas or otherwise applying the processing

solution to the region to be processed.

BRIEF DESCRIPTION OF THE DRAWINGS

The above and other objects, features and advantages of
5 the present invention will be more apparent from the
following description, taken in conjunction with
accompanying drawings in which:

Fig. 1 is a characteristic graph indicating variations
in pH and ORP values for solutions used in the present
10 invention and prepared by addition of electrolytes;

Fig. 2 is a schematic drawing showing a two-chamber type
electrolytic bath used for producing conventionally
electrolyzed water;

Fig. 3 is a schematic drawing illustrating conventional
15 equipment for generating electrolyzed water;

Fig. 4 is a schematic drawing showing a two-chamber
type electrolytic bath used for preparing electrolyzed
waters used in to the present invention;

Fig. 5 is a characteristic graph which indicates an
20 elapsing time-dependence of measured values in ORP since
immersion of an ORP (oxidizing/reducing potential) probe
into an electrolyzed water;

Fig. 6 is characteristic graph showing cleaning effects
of colloidal silica;

25 Fig. 7 is characteristic graph illustrating cleaning

time-dependence of colloidal silica;

Fig. 8 is characteristic graph indicating an effect for removing natural oxide film on GaAs;

Fig. 9 is a characteristic graph showing cleaning time-dependence of removal of inorganic particles;

Fig. 10 is a characteristic graph illustrating cleaning time-dependence of removal of natural oxide film on GaAs;

Fig. 11 is a characteristic graph indicating cleaning time-dependence of removal of colloidal silica on a metal;

Figs. 12A and 12B are a characteristic graph showing a cleaning solution dependence of effects for removing chlorine residual on the surface and a characteristic graph showing a processing time dependence of removal of chlorine residual on the surface, respectively;

Fig. 13 is a characteristic graph illustrating sheet resistances measured on silicide films;

Fig. 14 is a characteristic graph indicating a processing time-dependence of Cu concentration residual on a surface;

Fig. 15 is a Cu concentrations residual on wafer surfaces after processing in solutions obtained by addition of Cu at different concentrations;

Fig. 16 is a characteristic graph showing an effect for removal of Fe residual on a surface;

Fig. 17 is a characteristic graph illustrating a number

of adhered particles for showing an effect for removal;

Fig. 18 is a characteristic graph illustrating processing time-dependence of surface Cu concentration;

Figs. 19A and 19B are characteristic curves indicating
5 processing solution dependence of photoresist residues and
of photoresist residues, respectively;

Fig. 20 is a characteristic graph showing processing
solution dependence of etching velocity in GaAs;

Figs. 21A and 21B are a characteristic graph showing
10 processing solution dependence of removal effect of photo-
resist residue and a characteristic graph showing processing
time-dependence of residual photoresist quantities removed,
respectively; and

Fig. 22 is a Characteristic graph showing gate oxide
15 breakdown field distribution of MOS capacitors.

PREFERRED EMBODIMENTS

A method for producing electrolyzed water will be de-
scribed first. It is described, for instance, in A Handbook
20 for the Electrochemistry, 4th Press published in 1985, P.
277 that there exist two types of electrolyzing systems for
producing electrolyzed water, a two-chamber electrolyzing
system which is used for general purpose use and a three-
chamber electrtolyzing system which is capable of
25 electrolyzing even de-ionized water. Here, the two-chamber

electrolyzing system is detailed with reference to a schematic drawing of electrolytic bath shown in Fig. 4. Fig. 4 is basically identical to the figure shown in JP Patent Application No. 5(1993)-105991. An aqueous solution
5 401 added with a minute amount of supporting salts is transported from a reservoir (not shown in Fig. 4) into an electrolytic bath 400. An anode 402 and a cathode 403 are installed in corresponding one of chambers 408 and 409 of the electrolytic bath 400, being separated from each other
10 by an ion exchange film (a cationic membrane) 407 made of fluorinated compounds. The distance between the anode 402 and cathode 403 installed in each of the chambers 408 and 409 separated by the ion exchange film 407 is less than 1 cm. A DC voltage (2-50 V/cm) is applied therebetween.
15 Some species of supporting electrolytes which have scarcely ill-affects on semiconductor device characteristics are included in the aqueous solution 401 at a minute amount (8×10^{-2} - 2×10^{-5} mol/l) to raise an electrolyzing efficiency of de-ionized water. Addition of those electrolytes at a
20 minute amount remarkably increases electric conductivity of the aqueous solution 401 and is important for raising an electrolyzing efficiency.

It is considered that the electrolytes to be added into the aqueous solution should not include any metal because
25 the semiconductor wet processings are ill-affected by any

metallic contamination. It is found that ammonium chloride, ammonium acetate, ammonium fluoride, ammonium nitrate, ammonium bromide, ammonia iodide, ammonium sulfate, ammonium oxalate, ammonium carbonate, ammonium citrate, ammonium formate, hydrochloric acid and aqueous ammonia are valid as electrolytes used for this purpose, which will be described in detail later by citing practical embodiments of semiconductor wet processings. Similarly, combination of an adequate selection and an adequate mixing of the recited electrolytes will be presented later in accordance with the process as desired.

As shown in Fig. 4, the two-chamber electrolyzing system employed by us has two chambers 408 and 409 separated by an ion exchange film 407 and Pt electrodes 402 and 403 allocated to respective chambers 408 and 409, Pt electrodes 402 and 403 scarcely exhibiting chemical reactions with the electrolyzed waters as produced inside the chambers 408 and 409. Carbon, especially glassy carbon or RuO_2 may be used as electrode materials instead of Pt. It is unnecessary to apply an identical material to an anode and a cathode electrodes. It is allowable, for instance, to select Pt as a material for the anode electrode 402 which is immersed in an acidic solution while carbon as a material for the cathode electrode 403 which is immersed in an alkalic solution.

To utilize electrolyzed waters, a DC voltage is applied between the electrodes 402 and 403 so that hydrogen gas and oxygen gas are produced in the cathode chamber 409 and anode chamber 408, respectively, and liquids extracted from two chambers 408 and 409 are independently collected. The DC voltage as applied ranges from about 2 to about 50 V depending on concentration of the electrolyte as added into the de-ionized water and on an initial condition for electrolysis.

When electrolysis starts, H^+ ions are attracted to the cathode 403 and accept electrons from the cathode to liberate H_2 gas in the cathode chamber 409, resulting in an accumulation of OH^- ions in accordance with reduction in number of H^+ ions. Accordingly, the cathode water 405 staying in and flowing from the cathode chamber 409 exhibits alkalic and has a reducing activity because of existence of hydrogen of active base generated from the cathode 403. Due to a similar reason, OH^- ions are attracted to the anode electrode 402 and electrons are peeled-off in the anode chamber 408 by the anode electrode 402 to liberate O_2 gas in the anode chamber 408. Accordingly, the anode water 404 staying in and flowing from the anode chamber 408 exhibits acidic because of existence of excess H^+ ions in accordance with reduction in OH^- ions. The anode water 404 has further an oxidizing activity because of generation of O_2 and O_3

gases. Especially when an aqueous solution 401 containing the electrolytes recited in the present invention is electrolyzed, O_3 quantity increases as compared with the case when no electrolyte is added. On the other hand, when
5 halogen is added as an electrolyte, oxoacids (if the halogen atom is chlorine, it will be $HClO$, $HClO_2$, $HClO_3$ etc.) is formed and the oxidizing activity thereof is more remarkable.

Next, an embodiment of the present invention will be
10 described wherein electrolyzed waters are applied to concrete semiconductor wet processings. Here, pH and ORP (oxidizing/reducing potentials) values which will be cited in the following embodiments are defined. The pH values as recited in the present invention are measured on the basis
15 of electrochemical procedures by employing a pH meter available in the market, not measured by litmus papers. As shown in "A New Science of Water and Application Technologies", P. 193 presented by Mr. Sumita, pH values differ significantly between values measured by pH meters
20 and those by litmus papers. An experiment performed in the present invention indicated that an anode water and a cathode water exhibiting 2 and 9.5 in pH value, respectively, when measured by a pH meter, exhibited 4 and
7.5 in pH value, respectively, when measured by litmus
25 papers. Although sufficient theoretical reason why the

difference arises has not been found yet. pH values recited hereinafter are represented in terms of values measured by a pH meter because the pH values which indicate one aspect of characteristics of electrolyzed waters vary significantly when measured on the basis of electrochemical procedures. ORP values are measured by employing silver/silver chloride electrodes. Incidentally, it is well known that silver chloride electrode provides about +220 mV higher values as compared with those measured on the basis of a standard electrode.

On the other hand, it requires a certain period of time elapsing since immersing a measuring probe into a solution to obtain stationary pH and ORP values. Fig. 5 shows elapsing time dependence of measured ORP values since measuring probes are immersed into the solutions. Two time-dependence curves shown in Fig. 5 indicate a difference between the first curve A of ORP measured just after electrolysis and the second curve B of ORP measured after 12 hours has elapsed since electrolysis. It is found that pH and ORP values saturate immediately (converges to stationary values) in the solution immediately after electrolysis while it takes a long period of time to induce saturation in the solution for which a long period of time elapsed since electrolysis. It takes a long period of time for saturation in an ORP value, resulting from a low reaction speed

of the electrolyzed water for which a long period of time elapsed since electrolysis. In other words, there is only a small wet processing effect in such electrolyzed waters within a certain time period. It was found that effectiveness of a wet processing (for instance, a cleaning effect) enlarges with a decreasing time to saturation, and electrolyzed water immediately after the electrolysis provides a larger effectiveness even if two electrolyzed waters exhibit similar pH and ORP values to each other. Here, pH and ORP values measured after 1 minute passed since immersion of the probe into the solutions are employed in the description of the present invention, although pH and ORP values may be generally defined by saturated values.

Next, the present invention will be described with reference to actual application of electrolyzed waters to wet processings .

Firstly, characteristics of anode water and cathode water obtained by electrolysis will be detailed. The characteristics of anode and cathode waters obtained by electrolysis depends on the characteristics of the electrolytes added prior to the electrolysis. Addition of electrolyte is effective for reduction in resistivity during electrolysis while selection of electrolytes is proven capable of controlling ORP values. Fig. 1 shows changes in pH of de-ionized (ordinate) waters which include three

species of electrolytes (ammonium chloride, ammonium acetate and hydrochloric acid) at 0.05 weight (wt) percent (%) and in ORP (absicca) value, during electrolysis. The electrolysis is performed in a two-chamber type while a porous membrane is adopted as a separating film.

It is recognized that an electrolysis induces a high oxidizing water on the anode side while a high reducing water on the cathode side. Comparison among three species of electrolytes clarifies that an electrolyte including chlorine ions generates an anode water having a large ORP value while an electrolyte including ammonium produces a cathode water having a small ORP value (a large reducing activity). Beside chlorine, bromine and iodine are recognized to have a similar effect as electrolytes for enlarging ORP values of an anode water. Accordingly, it is advantageous in obtaining an anode water having a high oxidizing activity to employ salts such as ammonium chloride as an electrolyte beside hydrochloric acid, bromine solution, iodine solution etc.

On the other hand, it is advantageous in obtaining a cathode water having a small ORP value (for instance, -800 mV), namely a large reducing activity, to employ salts such as ammonium chloride, ammonium acetate, ammonium fluoride, ammonium nitrate, ammonium bromide, ammonium iodide, ammonium sulfate, ammonium oxalate, ammonium carbonate.

ammonium citrate, ammonium formate etc. as electrolytes beside aqueous ammonia.

There exist an optimum selection of electrolytes for performing a specified wet processing most adequately, although the electrolyzed water obtained by electrolysis of
5 a solution wherein the many electrolytes mentioned above are added operates effectively during various kinds of semiconductor wafer processing. As shown later in some embodiments, an electrolyzed water scarcely containing
10 chlorine ions exhibits a more remarkable effect because a wet processing after dry etching performed in an environment containing chlorine gas is generally directed to eliminating chlorine ions. Accordingly, ammonium acetate etc. can be
15 said preferable as an electrolyte instead of ammonium chloride.

A high ORP value measured in an anode water or a low (a largely minus) ORP value measured in a cathode water has not been obtained without electrolysis up to now. ORP values of chemicals generally used for semiconductor processings are
20 measured by employing silver/silver chloride electrodes at room temperature. Comparison conducted at condition of 0.005 mol/l indicates that ORP values are obtained at 550 mV by hydrochloric acid, 500 mV by hydrofluoric acid, 580 mV by sulfuric acid, 400 mV by hydrogen peroxide aqueous solution
25 and 80 mV by aqueous ammonia, while up to about 1200 mV by

anode waters and down to about -850 mV by cathode waters in ORP value. Accordingly, it is clear that the electrolyzed water exhibits specific characteristics which have not been obtained by combination between conventional chemicals.

5 Next, application of electrolyzed waters to semiconductor surface processings will be described in which it is focused on a step for wet etching by employing cathode waters. An aqueous solution is prepared by addition of ammonium chloride at a concentration of 0.002 mol/l into de-
10 ionized water, then provided into an electrolytic bath, and electrolyzed to provide a cathode water having -800 mV in ORP value ("+" sign means oxidizing while "-" sign means reducing) and 9.8 in pH value. When a silicon substrate is dipped into the cathode water, Si reacts with OH radicals
15 to form hydroxides, thereby effecting an etching proceeding. An etching rate up to about 50 angstrom/min, which is satisfactory in a practical production of semiconductor device, is attained when temperature of the cathode water is kept at about 65°C.

20 Furthermore, the cathode water-induced etching is very convenient to a selective etching wherein a SiO_2 film is employed as a mask. It is because the etching of silicon proceeds at a rate of 50 angstrom/min while an etch rate of the oxide remains below 0.5 angstrom/min, which raises the
25 selectivity up to more than 100. The etching rate of

silicon increases with an increase in quantity of ammonium chloride added into de-ionized water while showing a tendency to saturation, finally saturating when the added quantity approaches 0.08 mol/l. As described above, an
5 etch-rate in an electrolyzed water increases with an increase in an added quantity of ammonium chloride while a plain ammonium chloride aqueous solution that has not been subjected to any electrolysis does not exhibit any etching reaction no matter how much the concentration may be
10 increased, which verifies the specific effects inherent to the electrolyzed water.

A plain aqueous ammonia having a concentration of 0.002 mol/l exhibits 9 and +20 mV in pH and ORP values, respectively. The aqueous ammonia, if used instead of a
15 neutral ammonium chloride solution, provides at most 5 angstrom/min in an etch-rate of a Si wafer, which means that an electrolyzed water containing ammonium chloride at a concentration similar to that of aqueous ammonia exhibits a high etch-rate more than ten times that of the aqueous
20 ammonia. Namely, the electrolyzed water provides an etch-rate satisfactorily applicable to practical treatments and can replace the conventional etching treatments which have been performed by heating up to about 75°C of the conventional chemicals such as a mixed acid consisting of
25 hydrofluoric acid, nitric acid and glacial acetic acid.

aqueous ammonia-hydrogen peroxide mixture
($\text{NH}_4\text{OH}:\text{H}_2\text{O}_2:\text{H}_2\text{O}=1:4:20$, referred to as APM hereinafter),
choline solutions, KOH solution etc.

Moreover, the APM solution which has been applied to a
5 selective etching of silicon employing a SiO_2 film as a mask
has at most between one and two in a selectivity, i.e., in a
ratio of etch-rate of Si to etch-rate of SiO_2 , which fact
requires paying close attention to the application and
control to the wet processing. Application of the cathode
10 water enables a satisfactory treatment effect on the main
surface of a Si substrate which is exposed on the bottom of
a contact-hole, which in turn enables an electrode formation
onto a cleaned surface, thereby providing remarkable
increase in processing yield. Processes such as those
15 require a considerably slow etch-rate, which is easy of
attainment through decrease in additive quantity of ammonium
chloride.

A cathode water having a slow etch-rate range is
applicable to removing inorganic particles residual on a
20 silicon substrate. For example, an embodiment applied to
removing colloidal silica adhered onto a Si substrate which
has been subjected to CMP (chemical-mechanical polishing)
will be described below. Fig. 6 shows a cleaning effect
attained by a ten minute overflowing of a cathode water
25 having -720 mV and 8.2 in ORP and pH values which has been

prepared by electrolysis of an electrolytic solution including ammonium chloride at concentration of 5×10^{-5} mol/l, in comparison with conventional method using an APM solution. The result indicates that colloidal silica remained at more than 2000 particles/wafer prior to treatment reduced down to 80 particles/wafer. It is an excellent result as compared to the result of 100 particles/wafer which is attained by the conventional APM solution. Hence, employment of cathode water reduced concentration in chemicals and improved operational safety. Cathode waters having ORP values less than -700 mV and pH values more than 8 are especially effective for removing those inorganic particles. Electrolyzed waters obtained from solutions including ammonium chloride or ammonium acetate only at a rate of 2×10^{-5} mol/l have also enough effectiveness. This cathode water treatment is employed to remove particles by a minute amount of etching a silicon surface. Simultaneously, the cathode water exhibited an advantage that particles are difficult of re-adhesion onto the silicon substrate surface in the cathode water.

Furthermore, a cathode water produced from electrolytes added by an extremely minute amount ranging from about 1×10^{-6} to about 1×10^{-5} mol/l is also effective for removing through reducing activity a natural oxide film which is formed on the silicon surface and would frequently offer

problems. It is preferable to treat the substrate with an approximately neutral cathode water having an ORP value less than -500 mV and a pH value between 7 and 8 and warmed up to about 53°C. When treated in a cathode water having -700mV in an ORP value and 8 in a pH value, hydrogen atoms which terminate the dangling bonds located on the surface of a silicon substrate existed stably for more than twelve hours, which certifies suppression of re-growth of the natural oxide film.

Conventional procedure employing diluted hydrofluoric acid solution for removing the natural oxide film has several hours of an effective period of time for suppression of re-growth of the natural oxide film. The cathode water treatment according to the present invention not only lengthens the duration period for hydrogen termination but also can avoid the usage of hydrofluoric acid known as a dangerous chemical. Moreover, the cathode water treatment has a great advantage as compared with the diluted hydrofluoric acid solution, that it can remove only a natural oxide film even in a case when the natural oxide film exists on the selectively exposed silicon surface, such as on the bottom surface of a contact hole, or in a case when Al and SiO₂ co-exist therewith on a wafer surface.

In foregoing paragraphs, a cathode water obtained by hydrolysis of an aqueous solution obtained by addition of

either ammonium chloride or ammonium acetate at a concentration ranging from 0.1 to 2×10^{-5} mol/l has been described as to application to treatment of Si surface by the cathode water. In those paragraphs, effectiveness of a cathode water having an ORP value less than -500 mV and a pH value larger than 7 is clarified. Hydrogen-bubbling of the cathode water to dissolve hydrogen gas into the cathode water enhanced a reducing activity of the cathode water, raised a removing efficiency for inorganic particulates, reduced a treatment period of time (refer to Fig. 7) and enlarged the suppressing period of time for re-growth of a natural oxide film up to more than 24 hours. Measurement of dissolved hydrogen concentration after hydrogen-bubbling for about a minute clarified a concentration of 1.3 ppm in dissolved hydrogen, which is almost a saturated value at room temperature. H_2 -bubbling of the cathode water improved an etching uniformity of silicon and, consequently, improved surface smoothness of the silicon after etching. The reason why the etching uniformity is attained is considered due to the fact that the activity of the cathode water as a reductant was improved by the hydrogen-bubbling.

On the other hand, addition of H_2O_2 into the obtained cathode water enhanced an oxidizing activity, and suppressed an etch-rate of a silicon substrate, resulting in effecting an etching proceeding substantially without increase, in

surface rough or without increase in a removing efficiency of inorganic particulate contaminants. Effectiveness was confirmed at the condition wherein the quantity of H_2O_2 to be added ranges between a quantity similar to that of the electrolyte added for electrolysis and a quantity one digit smaller than that. UV (ultra-violet ray) irradiation as combined therewith further raised the removing efficiency.

The cathode water as described above is also applicable to removing inorganic particles and natural oxide films located on compound semiconductor substrates such as GaAs, InP, ZnSe etc. beside silicon. For that purpose, it is effective to use a cathode water having a pH value ranging from 7 to about 9 and warmed up to about 70°C. For instance, a cathode water having an ORP value less than -750 mV and a pH value of 8.7, which is obtained on the cathode chamber by electrolysis of the solution including ammonium acetate of 1×10^{-4} mol/l as an electrolyte, reduces density of 20000 particles/wafer in colloidal silica, which had been subjected to forced adhesion onto a GaAs substrate, down to less than 100 particles/wafer. It also reduced signal intensity of GaO observed by AES (Auger Electron Spectroscopy) analysis on a wafer surface down to the value less than a tenth of that before treatment (refer to Fig. 8).

On those occasions, H_2 gas-bubbling of the cathode

water for increasing the activity thereof as a reductant could further enhance removing efficiency for both inorganic particles (refer to Fig. 9) and natural oxide films (refer to Fig. 10). Up to now, organic solvents have mainly been employed to remove inorganic particles on a substrate surface while DHF ($\text{HF}:\text{H}_2\text{O}=1:100$) etc. have mainly been used to remove natural oxide films. Enlargement in field of application of the cathode waters remarkably reduces quantities of hydrofluoric acid and organic solvents as consumed.

Here, another embodiment will be described wherein a cathode water is applied to removing surface particles from semiconductor substrates. The cathode water is alkaline and active as a reductant while exhibits an etching activity to any materials no matter whether they may be metallic (silicidic) or insulating. The cathode water is suitable for removing such particles, because zeta potentials of both silicon and particles assume an identical sign (minus) in an alkaline solution which induces a repulsive force between the silicon and the particles, resulting in difficulty of particle adhesion no matter whether the particles may be inorganic or organic. A cathode water having -820 mV in an ORP value and 10.5 in a pH value, which is obtained from electrolyte containing 6.5×10^{-3} mol/l of ammonium acetate, reduced polystyrene particles adhered onto metallic (silicidic) or insulator films from an 3000 particles to

less than 100 particles. It also reduced colloidal silica on a metal (silicide) and insulator films from 30000 particles to less than 100 particles. On that occasion, bubbling for dissolving H_2 was also effective. Fig. 11 shows that colloidal silica can be effectively removed in a short period of time.

Up to now, a mixed liquid of $NH_4OH:H_2O_2:H_2O=1:1:5$ etc. warmed up to $70-90^\circ C$ have been used for cleaning treatment or a high pressure blowing jet of de-ionized water onto a substrate has been applied, in order to remove contaminations of inorganic and organic particles adhered onto a metallic (silicidic) or an insulator film. Although the latter is effective for quantity reduction of consumed chemicals similarly to the present invention, they have many disadvantages from the industrial point of view that wafer fractures due to the high pressure jet of de-ionized water blown onto substrates and that a batch cleaning operation of wafers is difficult. The use of cathode water has solved such problems as those.

A cathode water having an ORP value less than -700 mV and a pH value exceeding 7, which is obtained by electrolysis of an aqueous solution prepared by addition of ammonium acetate at a concentration ranging from 1×10^{-1} to 2×10^{-5} mol/l, is effective for removing inorganic and organic particles as described above. Application of the

cathode water warmed up to 70°C can further remove even rigidly adhered organic substances such as photoresist films.

Embodiments for processing semiconductor wafers will be described hereinafter, wherein weakly alkaline cathode waters exhibit a specific activity. Up to now, only an elaborate treatment in a de-ionized water warmed around 70-90°C has been recognized as effective for removing ionic residues adhered onto a silicon substrate, a GaAs substrate, a metallic film, an insulator film and a mixture of those after a dry etching step. The conventional wet processing generally required a treatment for a long time in a trial and error manner.

Application of a cathode water having both a weak alkalinity of about 8 in pH value and an activity as a reductant is effective for removing ionic residues as described above. On that case, only ionic impurities can be removed by a reducing reaction while substantially without etching any of silicon, compound semiconductors such as GaAs, metal, insulator films etc. Figs. 12A and 12B indicate evaluation results by hydrothermally extracted ion-chromatography of the amount of chlorine ion residual on a surface of a silicon substrate which has been subjected to sputter-deposition of an Al film and to a plasma-etching in a mixed gas including chlorine ions. The cathode water (ORP:-800

mV, pH:8.9) obtained by electrolysis of an electrolyte including ammonium acetate at 2×10^{-4} mol/l is employed as a cleaning solution in the method according to the present invention. The cleaning procedure employing the cathode
5 water reduced quantity of chlorine residual on the silicon substrate by about a hundredth of that the conventional cleaning procedure employing de-ionized water warmed up to around 70-90°C has attained, as shown in Fig. 12A. Furthermore, it is found that an enough cleaning effect may
10 be obtained if a liquid temperature of the cleaning solution is higher than room temperature of about 25°C.

The removing efficiency of residual chlorine is improved by hydrogen-bubbling which enhances the reducing activity. On the other hand, addition of a minute amount
15 of sulfuric acid instead of hydrogen-bubbling further enhances the removing efficiency of chlorine. Sulfuric ions and phosphoric ions are known to exhibit a strong reducing activity in alkaline solutions. Fig. 12B illustrates a result wherein sulfuric acid is added as much as about a
20 hundredth of the quantity of electrolyte added before electrolysis. The validity of sulfuric acid addition was confirmed at a molar concentration ranging between about a tenth and about a five hundredth of the concentration of the electrolyte as added before electrolysis, because the liquid
25 characteristic should be kept alkaline while the quantity of

sulfuric ions should be ensured to remain at a certain extent.

Cleaning by use of a cathode water having -750 mV in ORP value and 8 in pH value and containing an electrolyte including ammonium acetate at 6.5×10^{-5} mol/l can reduce surface concentrations of ionic residues both on metals (F^- , Br^- , Cl^- etc.) and on insulator films (Cl^- , SO_4^{2-} etc.) down to between 1/10 and 1/100 of the initial concentration. The cathode waters described above are also applicable both to chlorine removal out of GaAs and to sulfur removal after etching in solutions including sulfuric acid, substantially without modification of the solutions.

Another embodiment as to GaAs will be described further, in which treatment employing a cathode water having -700 mV in ORP value and 8 in pH value, which is prepared on the cathode chamber from an electrolyte including ammonium chloride at 1.9×10^{-5} mol/l, reduced quantity of Cl residual on a GaAs substrate having 6 inches in diameter down to less than 10 ng (nano gram).

Effectiveness of the cathode water has been described for removing ionic residues hereinbefore. Its effectiveness is specifically characterized by being applicable to removal of naturally grown oxide films on the materials, such as Al and silicide, which have only poor chemical durabilities. Until now, physical procedures such as Ar-

plasma sputtering have been employed for removing natural oxide films on those materials. However, the physical procedures induced some damages on exposed surfaces of silicon substrates and generated charge building-up phenomena, resulting in degradation of breakdown voltage in insulator films.

On the contrary, employment of a cathode water can remove natural oxide films out of interconnection surfaces, substantially without the problems as described above. Fig. 13 demonstrates sheet resistance measured for a silicide layer after subjected to processings for removing natural oxide films. If a natural oxide film formed on a silicide layer can satisfactorily be removed, the sheet resistance as determined will exhibit a low value. Treatment employing a cathode water having -800 mV in ORP value and 8.5 in pH value, which is prepared by electrolysis of an aqueous solution including ammonium chloride at 9×10^{-3} mol/l, reduced the sheet resistance of about $70 \mu\Omega/\text{cm}^2$ prior to treatment down to about a fifth. It is proven that the conventional technologies can be enough replaced by a cathode water treatment according to the present invention, in view that Ar-plasma etching exhibits only a reduction to about 1/2.

As to removal of ionic impurities, it is preferred to use the cathode water having an ORP value less than -700 mV

and a pH value ranging from 7 to 9 and obtained by electrolysis of an aqueous solution including ammonium acetate at a concentration ranging between 8×10^{-2} and 2×10^{-5} mol/l for removing ionic impurities substantially without etching various species of materials as described above. The range, however, is enlarged if the processing allows etching of the underlying materials to some extent, and even cathode waters having ORP values less than -120 mV and pH values exceeding 7 can be used.

Hereinafter, other embodiments will be detailed wherein anode waters are applied to processings for removing metallic contaminants out of semiconductor wafers. A semiconductor manufacturing process frequently requires wet processings for removing metallic contaminants (Fe, Cu, Al, Ni etc.). The reason therefore is that a semiconductive material contaminated with metals, especially with heavy metals, generates deep energy levels which acts as recombination centers of electrons and holes having large cross-sectional areas for capture, degrading electric characteristics of a semiconductor device.

Until now, solutions including strong acids have been employed as technologies for removing metallic contaminants on silicon substrates, metals and insulator films. For instance, cleaning solutions, such as a solution warmed around 100 to 150 °C and containing $H_2SO_4:H_2O_2=4:1$ (SPM) and

another solution warmed around 70 to 90 °C and containing
HCl:H₂O₂:H₂O=1:1:5 (HPM or SC-2). have been applied to
cleaning silicon substrates and insulator films, while HPM
etc. have been applied in the case of contaminants on a
5 metal. Similarly, it is well known that acids such as
sulfuric acid (for GaAs, InP etc.) and hydrochloric acid
(for GaAs etc.) have been employed for cleaning compound
semiconductors. Especially high grade chemicals have been
desired for the electronics industry use because almost all
10 of those conventional cleaning solutions include high
concentration of acidic chemicals, and removal of metallic
ions, such as iron ions, from those solutions, such as H₂SO₄
and HCl, has been difficult. Hence, conventional
processings in a solution including low grade chemicals for
15 removing metallic contaminants will effect the solution
themselves to act sources for metallic contamination.
Costs of chemicals required for removal of metallic
contaminants therefore rise and quantities of wasted high
concentration chemicals rise up to a vast amount. A system
20 for guaranteeing the safety during operation is also
required because the warmed chemicals are used in general.

Many problems described above will be substantially
solved if an electrolyzed water according to the present
invention is applied to processings for removing metallic
25 contaminants. An embodiment will be described for a

treatment using an anode water having an oxidizing potential larger than +700 mV and a pH value less than 4, which is obtained by electrolysis of an aqueous solution prepared by addition of either ammonium chloride or hydrochloric acid at a concentration between 8×10^{-2} and 10^{-3} mol/l. Fig. 14 shows quality analysis results, employing Atomic Absorption Spectroscopy, in concentrations of Cu adhered onto a surface of a silicon substrate, which has been subjected to a forced contamination by Cu ions, before and after cleaning processings.

Conventional methods employing treatments by cleaning solutions such as those called SPM and HPM in abbreviation are also shown therein. An anode water having +1200 mV in ORP value and 1.8 in pH value, which is obtained by electrolysis of an aqueous solution prepared by addition of ammonium chloride at 0.01 mol/l, was warmed up to about 70°C, and applied to treatment for five minutes, thereby reducing initial 10^{13} atoms/cm² in Cu concentration on a silicon substrate before cleaning to less than 10^{10} atoms/cm² and consequently providing cleaning effects not lower than that of the conventional processings. Application of the anode water to processings for removing metallic contaminants both on metal (silicide) and on insulator films also exhibited effective, resulting in reduction of Cu concentration from 10^{13} atoms/cm² to less

than 10^{10} atoms/cm² in both cases.

Moreover, addition of either chelating agents or acids into the anode water was effective for removing metallic contaminants as recited above. Chelating agents and acids
5 are both effective for avoiding re-adhering behaviors of dissolved metallic contaminants onto wafers because chelating agents and acids form comparatively stable compounds, as a result of being ionized by oxidizing reactions to form complex ions and then combined with me-
10 tallic ions. Namely, addition of a minute amount of chelating agents or acids into the anode water improves a stability in effectiveness for removing metallic contaminants by the anode water.

In case of wet processings of a wafer, quantity of
15 metallic ions dissolved in solutions increases while removing efficiency of contaminants reduces, with increasing wafer number to be processed. In this case, addition of either chelating agents or acids into the cathode water increased the wafer number to be processed by two or three
20 times, while keeping the removing effect of the metallic contaminants at a certain level. Employment of chelating agents such as aqueous ammonia, ethylene diamine or EDTA (Ethylene Diamine Tetra-Acetic acid) or acids, such as hydrochloric acid, formic acid and nitric acid, which
25 include comparatively less impurities, when used as an

additive, proved that a common addition effect exists in an addition quantity ranging from 10^{-2} to 10^{-4} mol/l, providing somewhat different effects depending on the conditions whether or not an electrolyte is added during preparation of the anode water and on the species of chelating agents or acids used therein.

An increase in additive quantity exceeding 10^{-2} mol/l induces variations in solution characteristics such as an ORP value, resulting in a tendency to rather degrade the cleaning effect. On the other hand, reduction in additive quantity to less than 10^{-4} mol/l reduces the additive-induced effect, resulting in approaching the effect as obtained by a plain anode water.

An anode water is also applicable to processings for removing metallic contaminants (Fe etc.) on a naturally grown oxide film as well as included in naturally grown oxide films and thermally grown oxide films. Until now, a natural oxide film has been removed by BHF ($\text{HF} + \text{NH}_4\text{F} + \text{H}_2\text{O}$), DHF ($\text{HF} + \text{H}_2\text{O}$) solution etc., whereby metallic contaminants on and in the oxide films have been removed. Those conventional technologies, however, have encountered with problems that minute particles re-adhere onto a silicon substrate surface after processings and a metal (for instance, Cu), of which ionization tendency is less than that of silicon, rather deposit from the solution, if the minute particles are

contained therein, onto the silicon substrate, beside the problem residing in applying heavily concentrated chemicals.

As countermeasures to the above problems, a processing employing an anode water having an oxidizing potential
5 larger than +700 mV and a pH value less than 4, which is obtained by electrolysis of an aqueous solution prepared by addition of ammonium chloride or hydrochloric acid as an electrolyte at a concentration ranging from 8×10^{-2} to 10^{-3} mol/l, is applied to the silicon substrate, after the anode
10 water is combined with hydrofluoric acid to obtain a cleaning solution containing hydrofluoric acid at a concentration ranging from 10^{-2} to 10^{-3} mol/l.

The cathode water by itself scarcely has an activity to etch off oxide films. Addition of hydrofluoric acid,
15 however, enables etching-off oxide films as well as removing metallic impurities included in the natural oxide film. Treatment proceeds with an etching reaction together with an oxidizing reaction on the surface of the silicon substrate, which hinders the crystalline surface of silicon
20 from exposing to the cleaning solution, resulting in neither particle adhesion nor Cu deposition that the conventional processings have encountered with.

Fig. 15 indicates analysis results, employing atomic absorption spectrophotometry, of Cu concentration on a wafer
25 surface which has been subjected to processings in cleaning

solutions added with certain quantities of Cu. Processings in the conventional BHF solution increase Cu deposition quantity onto a Si substrate with increasing Cu additive quantity, while processings in the anode water added by hydrofluoric acid keep Cu deposition quantity less than 10^{10} atoms/cm², independently of Cu additive quantity. Furthermore, even metallic contaminants such as Fe existing in a natural oxide film can be removed effectively (refer to Fig. 16).

Fig. 17 shows adhesion quantities of minute particles onto a silicon substrate. A conventional processing in BHF solution induces particle adhesion of about from 300 to 400 particles/wafer onto a silicon substrate. On the other hand, an anode water having +1200 mV in ORP value and 1.8 in pH value, which is obtained by electrolysis of an aqueous solution prepared by addition of 10^{-2} mol/l of ammonium chloride, was applied for treatment after being added with hydrofluoric acid at a concentration of 0.05 mol/l, to thereby obtain a reduction of a number of minute particles as adhered down to about a tenth. A similar effect was also obtained by processing in an anode water prepared by electrolysis of an aqueous solution including ammonium chloride or hydrochloric acid at a concentration ranging from 10^{-1} to 10^{-3} mol/l, added with hydrofluoric acid beforehand at a concentration ranging from 10^{-1} to 10^{-2}

mol/l. When ammonium fluoride is used as an electrolyte, a similar effect was obtained without addition of hydrofluoric acid.

5 In the embodiments described above, addition of H_2O_2 at a concentration ranging from 10^{-1} to 10^{-2} mol/l or O_3 -bubbling can efficiently remove metallic contaminants located on silicon surfaces, metals and insulator films (refer to Fig. 18).

10 As described above, processings according to the present invention can remarkably reduce concentration of chemicals as used and can provide an enough effect even in a low processing temperature, so that metallic impurities on semiconductor substrates can be removed efficiently, while operational safety for workers is guaranteed.

15 Hereinafter, description will be concentrated on removal of organic substances on a semiconductor wafer by employing an anode water.

Many photolithographic steps are conducted in a semiconductor device manufacturing process wherein steps for removing photoresist films are repeated. Removing organic materials including photoresist films adhered onto a wafer surface, such as one represented by a photolithographical step, is important for raising manufacturing yields. Until now, highly concentrated and warmed chemicals such as APM solution (70-90°C) or SPM solution (100-150°C) have been

20

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employed for removing organic contaminants located on silicon substrates and on insulator films as well as for removing metallic materials on the surface of organic films or in the organic films, while warmed SPM solution (about
5 130°C) has been employed for removing those materials located on metals (silicides). Removing organic materials by employing an anode water as first recited hereinbelow is based on oxidation-induced decomposition of organic materials and as effective as an alkaline cathode water,
10 which enables also removing organic materials through minute etching of silicon substrates, insulators and metals (silicides).

First, experimental results in removing organic contaminants on silicon substrates by employing an anode water
15 will be demonstrated. Processing in an anode water having +1200 mV in ORP value and 1.8 in pH value, which is obtained by electrolysis of an aqueous solution prepared by addition of ammonium chloride at 0.01 mol/l, provides an effect equivalent to those of the conventional processings for
20 removing organic materials. Processings according to the present invention reduce, as a matter of course, quantity of chemicals as used. Moreover, although enough rinsing steps in de-ionized water have been generally required in the conventional processings after using comparatively dirty
25 chemicals such as SPM solution, electrolyzed waters

according to the present invention reduces rinsing steps remarkably because the electrolyzed waters are basically diluted solutions.

Figs. 19A and 19B indicate resultant data experimented on removing photoresist residues. Ordinate of Figs. 19A and 19B represent remaining rates of photoresist residues in terms of a ratio of number of patterns in which an SEM inspection can detect any of photoresist residues to total number of patterns as inspected. No photoresist residue was identified after processing according to the embodiment on a silicon substrate which had been subjected to a cleaning procedure in the anode water, which indicated an excellent effect comparable to that of the conventional cleaning procedure in SPM solution.

Processing for removing organic residues, such as photoresist residues, by employing the anode water described above is also applicable to those on an insulator film. The anode water having +1200 mV in ORP value and 1.8 in pH value, which is same as those used in the case of silicon surface, can remove photoresist residues substantially completely. The extent of adhesion of organic materials can be evaluated by a wetting angle (contact angle) of de-ionized water. A clean silicon dioxide film exhibits a contact angle not higher than about 10 degree while the contact angle increased up to about 50 degree when

contaminated by organic materials. The contact angle decreased down to the value substantially as small as that of a clean silicon dioxide film after subjected to a cleaning processing in the cleaning solutions according to the present invention, which verified an excellent effect for removing organic materials compared with about 20 degree in a contact angle obtained by the conventional cleaning in SPM solution. In addition, the anode water is also effective for removing photoresist on metals (silicides).

10 The removing effect for organic materials as described above can be further improved by addition of a minute amount of oxidants, H_2O_2 , at a concentration between 0.1 and 0.01 mol/l into the anode water or by O_3 -bubbling in the anode water. A smaller time period is further attained when those processings are performed under a UV-irradiation. Those effects were also confirmed also about photoresist residues on insulator films.

20 The anode water processing is also effective for removing organic materials such as organic particles and photoresist residues remaining on compound semiconductor substrates such as GaAs, InP, ZnSe etc. beside silicon. The conventional procedures for removing organic materials remaining on compound semiconductor substrates have been performed by employing warmed (up to about 80°C) organic solvents. The reason therefore is that application of

25

acidic hydrogen peroxide as used for Si substrates will effect an etching reaction of the compound semiconductor substrates themselves. Even on that occasion, the anode water having a higher acidity exhibits an excellent effectiveness as well as in silicon processing. For instance, processing GaAs substrates in an anode water having 1080 mV in ORP value and 4 in pH value, which is obtained by electrolysis of an aqueous solution prepared by addition of ammonium chloride at 5×10^{-5} mol/l, can easily reduce organic particles (polystyrene particles) from 3000 particles/wafer down to about 50 particles/wafer.

As an example of removing photoresist residues and organic films, processings employing an anode water having 1000 mV in ORP value and 2 in pH value reduced photoresist residues to less than 10 ng/wafer of 6 inches and reduced residual quantity of organic films to less than 20 ng/wafer of 6 inches. Furthermore, on that occasion, O_3 -bubbling of the anode water could remove more effectively organic particulate such as contaminations, photoresist residues and organic films. In order to avoid an etching reaction in the case of compound semiconductor substrates such as GaAs, it is important not to enhance an oxidizing activity significantly. pH values larger than around 3-5 and ORP values larger than +600 mV are preferable in case of suppressing etching reaction, because strong acidity

accelerates etching reaction during removing various species of organic materials on a compound semiconductor.

On the contrary, an anode water exhibiting a strong acidity is useful for etching compound semiconductors such as GaAs, InP, ZnSe etc. Up to now, highly concentrated chemicals such as a mixed solution of $H_2SO_4:H_2O_2=5:1$ (by volume ratio), a mixed solution of $H_3PO_4:H_2O_2=5:1$ (by volume ratio) etc. have been employed for etching of them. According to the present invention, for instance, an anode water, warmed up to $65^\circ C$, having 1200 mV in ORP value and 1.9 in pH value, which is obtained by electrolysis of an aqueous solution prepared by addition of ammonium chloride at 0.01 mol/l, provides 80 nm/min in etch-rate of GaAs. The practical etch-rate is controllable either by enhancing an acidity of the anode water including ammonium chloride as an electrolyte through O_2 -bubbling to accelerate etch-rate or by addition of H_2O_2 to suppress etching reaction (refer to Fig. 20). A practical etch-rate was obtained at a condition of added quantity of ammonium chloride between 0.002 and 0.2 mol/l, an ORP value larger than +800 mV, and a pH value less than 3.

The present invention is effectively applied to removal of organic films on interconnections made of Al and metal silicide films which have poor durabilities against acidic and alkalic chemicals. Up to now, only organic chemicals

have been applicable to those processings and a vast volume of organic chemicals have actually been consumed. However, an electrolyzed water having only a weak oxidizing activity is now proven applicable.

5 For instance, wet processing in an anode water having +800 mV in ORP value and 5.5 in pH value, which is obtained by electrolysis of an aqueous solution prepared by addition of ammonium chloride at 10^{-5} mol/l as an electrolyte, lowered about 70 $\mu\Omega$ of a sheet resistance before treatment
10 down to about a tenth. This value verifies effectiveness of a cleaning treatment according to the present invention as compared with a fifth that the conventional cleaning treatment has attained. The validity of the cleaning treatment according to the present invention is understood
15 in view of the fact that an organic film existing on a metallic interconnection generally acts as an insulating film which induces a rise in a sheet resistance.

 Removing organic materials by employing anode waters have been demonstrated hereinbefore. However, cathode
20 waters can also remove organic materials. Employment of cathode waters having an oxidizing activity are also effective for removing organic contaminants and photoresist residues. When a cathode water is applied to removing organic materials on silicon substrates, metals and insulator
25 films, the silicon substrates, metals and insulator films

are etched, and further, zeta potentials have an identical sign (minus) both in the silicon substrates and in the particles, which generates a repulsive force between silicon substrates and the particles. Consequently, it induces an
5 extremely high removing efficiency because re-adhesion is difficult to occur.

As an embodiment for those kinds of treatments as described above, a cathode water was applied having an ORP value less than -700 mV and a pH value larger than 7, which
10 was obtained by electrolysis of an aqueous solution prepared by addition of ammonium acetate or ammonium chloride at a concentration between 0.1 and 10^{-5} mol/l. For example, a cathode water, warmed up to about 70°C, having -800 mV in ORP value and 10 in pH value, which was obtained by
15 electrolysis of an electrolytic solution including 6.5×10^{-3} mol/l of ammonium acetate, removed photoresist residues remaining both on insulator films and metals satisfactorily (refer to Fig. 21). On those cases, hydrogen-bubbling enhances reducing reaction, resulting in an improved
20 efficiency by about double in removing organic materials both on insulator films and metals (silicides). The removal of organic materials as described above is based on a positive application of alkalescency and a reducing activity both inherent to the cathode water.

25 The following is examples of processings utilizing both

an etching function for underlying substance inherent to cathode waters and oxidation-induced decomposing function for organic materials due to additive oxidant. For an example, removal of organic materials and photoresist residues both on a Si substrate will be shown. A cathode water having -650 mV in ORP value and 7.8 in pH value was prepared by addition of ammonium chloride at 2×10^{-5} mol/l and by electrolyzing thereof, following which H_2O_2 was added thereto at 0.1-0.01 mol/l as an oxidizing agent to obtain a processing solution. Immersion of a silicon substrate adhered with organic materials and photoresist residues into the processing solution could remove organic materials as effectively as on insulator film and on metals to reduce the organic quantity down to less than a tenth of that before cleaning. Addition of H_2O_2 presents effects for strengthening the oxidizing activity as well as for avoiding surface rough through suppressing excessive etching. Those effects are also attained by O_3 -bubbling, and enhanced by combination with UV-irradiation, resulting in, for example, a smaller time period for treatment.

As a somewhat peculiar example of application, a surface oxidation of a silicon substrate will be demonstrated. A surface treatment of the silicon substrate in a chemical solution including hydrofluoric acid generally exposes an active surface of single-crystalline silicon.

onto which minute particles and metals are liable to adhere. On the other hand, when a thermal oxidation is performed at a state wherein the single-crystalline surface of silicon is exposed, a surface rough of the substrate and an ununiform, naturally grown oxide film will generate to thereby degrade quality of the thermally grown oxide depending on insertion/extraction conditions of a furnace. As a result, problems of insulation failures may arise.

Here, application of electrolyzed waters solves those problems as described above. Application of electrolyzed waters according to the present invention is especially effective for post-treatment of processings in chemical solutions including hydrofluoric acid. Namely, rinsing of a silicon substrate is performed in an anode water having an ORP value larger than +700 mV and a pH value less than 4, which is obtained by electrolysis of an aqueous solution prepared by addition of ammonium chloride or hydrochloric acid at 0.1-0.001 mol/l as an electrolyte. Treatment in hydrofluoric acid itself is a process directed to removing metallic impurities, natural oxide films and organic impurities. Immersion into the anode water, however, provides a clean and stable natural oxide film formed on the silicon substrate surface.

Until now, rinsing in an ultra-pure (de-ionized) water has been performed for about five minutes after treatment in

BHF. A five minutes' rinsing was also performed after treatment in BHF, according to the present invention, by employing an anode water having +1200 mV in ORP value and 1.8 in pH value, which was obtained by electrolysis of an electrolytic solution including 0.01 mol/l of ammonium chloride. The technology according to the present invention reduced density of minute particles by less than a tenth as compared to the value about five hundreds or more particles/wafer residual on a substrate subjected to the conventional treatment.

Fig. 22 shows breakdown field distributions of gate oxide films for MOS capacitors formed by employing processings according to the present invention and by the conventional technology. Failures including metallic contaminant-induced B-mode failures and pin-hole-induced A-mode failures in oxide films which were encountered with the conventional technology are substantially eliminated.

Various species of processings employing electrolyzed waters have been described hereinbefore as to a variety of semiconductive wafers. Suitable species of electrolytes, suitable additive quantities, suitable pH and ORP values have been also described in accordance with the species of processings. As electrolytes to be added, ammonium chloride, ammonium acetate, hydrochloric acid etc. have been referred to in embodiments. Beside those, ammonium

fluoride, ammonium acetate, ammonium bromide, ammonium
iodide, ammonium sulfate, ammonium oxalate, ammonium
carbonate, ammonium citrate, ammonium formate and aqueous
ammonia are proven effective as far as have been confirmed
5 in experiments.

However, the purity of electrolyte is proven to provide
some effects on residues after wet processings. For ex-
ample, in a case when a specific metal is included in the
electrolytes at a certain amount, the metal is liable to
10 remain on a wafer after a wet processing. As to impurity
of chemicals, hydrochloric acid records a highest purity
while aqueous ammonia occupies a second position and chemi-
cals formed as salts have comparatively poor purities.
Among the electrolytes as recited above, ammonium fluoride,
15 ammonium nitrate and ammonium chloride exhibit comparatively
good purities. In view of this, detailed investigation has
been concentrated on chemicals having comparatively good
purities, and description will be focused thereon. The
chemicals should be selected out of hydrochloric acid,
20 aqueous ammonia, ammonium fluoride, ammonium nitrate,
ammonium chloride etc. from the standpoints of the present
chemical purities and the process steps applicable thereto.
Those limitations are, however, not inherent to those
chemicals by themselves, because other chemicals may be
25 expected to provide similar treatment effects so long as

purities of those chemicals are improved.

Preferable quantity of an electrolyte to be added to de-ionized water before electrolysis is proven to reside within a range between 0.08 and 2×10^{-5} mol/l. The
5 preferable upper limit of additive quantity is defined by an upper limit of electrolytic concentration wherein an electrolytic bath for low concentration use can pursue electrolysis. An improvement in equipment, however, may raise this upper limit. On the other hand, the preferable
10 lower limit of electrolytic concentration is defined by stability in characteristics of electrolyzed waters. This lower limit can also be lowered by improvement in equipment and even a lower electrolytic concentration may exhibit an actual effect depending on species of processings.

15 As to ORP and pH values, a region wherein pH value exceeds 7 and ORP value stays less than -120 mV, and another region wherein pH value stays less than 7 and ORP value exceeds +700 mV exhibit considerably excellent effectiveness on processing semiconductive wafers. This fact is
20 consistent with another fact that a remarkable characteristic nature of an electrolyzed water induces significant difference in ORP values between them and other aqueous solutions obtained by mere addition of an electrolyte. Consequently, the another fact confirms, as
25 experimentally verified, a next fact that electrolyzed

waters, of which ORP values stay between +600 mV and -120 mV around an ordinary value of +220 mV, do not exhibit a remarkable effect on processing semiconductive wafers.

Furthermore, oxoacid ions of about 10^{-3} mol/l detected
5 in an electrolyzed water including chlorine, bromine and iodine are considered substances which provide specific characteristics of electrolyzed waters. Oxoacid ions include ClO_x^- , BrO_x^- , IO_x^- . This finding indicates that a large amount of oxoacid ions have a close relation to effective
10 processings of semiconductor wafers.

Moreover, above embodiments are described as to solutions wherein H_2O_2 is added as an oxidizing additive, O_3 -bubbling is adopted for enhancement of an oxidizing activity and hydrogen-bubbling is introduced for enhancement
15 of a reducing activity, all of additives being added at least into either side of electrolyzed waters for providing a perturbation in characteristics of the electrolyzed waters. However, another solution wherein either Cl_2 or Br_2 gas is dissolved at a concentration ranging from 10^{-2} to 10^{-4}
20 mol/l has also exhibited a similar effect and, addition of hydrofluoric acid at a concentration ranging from 0.1 to 0.001 mol/l, as described before, is also remarkably effective especially if the processing is directed to removing the surface contaminants etc. in parallel with
25 removing a natural oxide film.

Furthermore, addition of an adequate quantity of H_2O_2 , O_3 , Cl_2 , Br_2 , hydrogen or hydrofluoric acid into at least either side of the electrolyzed waters exhibits an excellent processing effects specific to the electrolyzed water when the addition is performed into either side of the electrolyzed waters which have been obtained by electrolysis of an even plain de-ionized water. Each of the lower limits and upper limits in residual quantities of O_3 , Cl_2 , Br_2 and H_2 gases as well as in additive quantities of H_2O_2 , HF etc., corresponds to a minimum quantity wherein a specific effect for a semiconductor processing appears and a maximum quantity wherein any effect specific to the electrolyzed water cannot be obtained anymore while rendering an effect specific to electrolytic additives themselves dominant, respectively. To suppress the electrolyte and additive quantities in a low amount is preferable from the initial standpoint of reduction in chemical consumption. However, requirement for saving a processing time period makes the additive quantity approach the maximum limit. Even on that occasion, the maximum limit of the additives is preferable to stay at 0.1 mol/l, which makes it understood that processings according to the present invention can reduce the consumption in chemicals remarkably as compared to the chemical consumption in the conventional processings.

It is shown that wet processings by use of electrolyzed

active waters, limiting chemical consumption at most 8×10^{-2} mol/l, have remarkable effects for removing surface particles, for removing a surface natural oxide film, for etching etc. which exhibit no lower level than that the
5 conventional wet processings have.

Accordingly, concentrations of solute which have been used in strongly acidic and alkalic solutions or other ionic solutions of the conventional wet processings for manufacturing semiconductor devices can be reduced
10 remarkably. It is quantitatively clarified that the chemical consumption can be reduced by more than one digit at least on the most cases and more than four digits on specific cases as compared to the conventional, heavy chemical consumption, depending on species of processings.

15 Although amount of reduction in environmental load has not quantitatively been calculated, it is clear that a large load reduction for treatment of waste chemicals can be ensured even if an electric power consumption for applying voltages to water may be equivalent to a load for
20 consumption of concentrated chemicals. Moreover, metallic contaminants of heavy metals accompanying with concentrated chemicals and having a difficulty of removal from solutions are also proven avoidable for a clean environment. Together with the advantages, unmeasurable effects can be attained in
25 which securing safety for workers, dangers in

transportation, and costs therefore can be reduced.

Furthermore, electrolyzed water even having almost neutral character, so far as obtained by electrolysis employing a minute amount of a supporting electrolyte, has a surface oxidizing activity or a surface reducing activity after it has lost the electrolyzation effect, which fact attracts a new scientific attention for processing procedures of semiconductor wafers.

Each feature disclosed in this specification (which term includes the claims) and/or shown in the drawings may be incorporated in the invention independently of other disclosed and/or illustrated features.

The appended abstract as filed herewith is included in the specification by reference.

WHAT IS CLAIMED IS:

1. A method for processing a semiconductor substrate including consecutively: a first step of adding at least one electrolyte selected from a group consisting of ammonium chloride, ammonium acetate, ammonium fluoride, ammonium nitrate, ammonium bromide, ammonium iodide, ammonium sulfate, ammonium oxalate, ammonium carbonate, ammonium citrate, ammonium formate, hydrochloric acid and aqueous ammonia into de-ionized water at a concentration ranging from 8×10^{-2} to 2×10^{-5} mol/l; and a second step of electrolyzing said de-ionized water to prepare at least one ionized water.

2. A method for processing a semiconductor substrate as defined in Claim 1 further including a third step of adding at least one acid selected from a group consisting of chelating agents, hydrochloric acid, formic acid and nitric acid at a concentration ranging from 10^{-2} to 10^{-4} mol/l into said de-ionized water.

3. A method for processing a semiconductor substrate as defined in Claim 2 further including a fourth step of bubbling said ionized water with at least one gas selected from a group consisting of Cl_2 , Br_2 , I_2 and O_3 .

4. A method for processing a semiconductor substrate as defined in Claim 1, wherein said at least one ionized water includes an anode water, further including a third step of adding at least one chemical selected from a group consisting of hydrofluoric acid and ammonium fluoride at a concentration ranging from 10^{-1} to 10^{-3} mol/l into said anode water.

5. A method for processing a semiconductor substrate as defined in Claim 4 further including a fourth step of bubbling said anode water with at least one gas selected from a group consisting of Cl_2 , Br_2 , I_2 or O_3 .

6. A method for processing a semiconductor substrate as defined in Claim 1, wherein said at least one ionized water includes a cathode water, further including a third step of adding at least one acid selected from a group consisting of sulfuric acid and phosphoric acid into said cathode water at a molar concentration ranging from 1/10 to 1/500 of the molar concentration of said electrolyte as added.

7. A method for processing a semiconductor substrate as defined in Claim 6 further including a fourth step of bubbling said ionized water with H_2 gas.

8. A method for processing a semiconductor substrate as defined in Claim 1, wherein said at least one ionized water includes a cathode water, further including a third step of adding H_2O_2 into said cathode water at a molar concentration ranging between the molar concentration of said electrolyte
5 as added and 1/10 thereof.

9. A method for processing a semiconductor substrate as defined in Claim 8 further including a fourth step of bubbling said cathode water with H_2 gas.

10. A method for processing a semiconductor substrate including consecutively: a first step of electrolyzing de-ionized water to prepare an anode water; and a second step of adding at least one acid selected from a group consisting
5 of chelating agent, hydrochloric acid, formic acid and nitric acid at a concentration ranging from 10^{-2} to 10^{-4} mol/l into said anode water to provide a processing solution for processing a semiconductor substrate.

11. A method for processing a semiconductor substrate as defined in Claim 10 further including a third step of bubbling said ionized water with at least one gas selected from a group consisting of Cl_2 , Br_2 , I_2 and O_3 .

12. A method for processing a semiconductor substrate as defined in Claim 1, wherein said at least one ionized water includes an anode water, further including a third step of bubbling said anode water with at least one gas selected
5 from a group consisting of Cl_2 , Br_2 , I_2 and O_3 .

13. A method for processing a semiconductor substrate as defined in Claim 1, wherein said at least one ionized water includes a cathode water, further including a third step of bubbling said cathode water with H_2 gas.

14. A method for processing a semiconductor substrate including steps of ionizing de-ionized water to prepare a cathode water and bubbling said cathode water with H_2 gas.

15. A method for processing a semiconductor substrate by use of a processing solution containing oxoacid ions of at least one of chlorine, bromine and iodine at a concentration not lower than 10^{-3} mol/l.

16. A method for processing a semiconductor substrate substantially as herein described.

Relevant Technical Fields

- (i) UK Cl (Ed.N) C7B (BDAJ, BDBC); H1K (KLXC, KLECX)
 (ii) Int Cl (Ed.6) C02F 1/46; H01L

Databases (see below)

- (i) UK Patent Office collections of GB, EP, WO and US patent specifications.

- (ii) ONLINE: WPI

Search Examiner
 D SUMMERHAYES

Date of completion of Search
 14 JUNE 1995

Documents considered relevant
 following a search in respect of
 Claims :-
 1-9

Categories of documents

- X:** Document indicating lack of novelty or of inventive step. **P:** Document published on or after the declared priority date but before the filing date of the present application.
- Y:** Document indicating lack of inventive step if combined with one or more other documents of the same category. **E:** Patent document published on or after, but with priority date earlier than, the filing date of the present application.
- A:** Document indicating technological background and/or state of the art. **&:** Member of the same patent family; corresponding document.

Category	Identity of document and relevant passages	Relevant to claim(s)
X,P	EP 0605882 A1 (NEC) see particularly column 4 line 58 to column 5 line 14	1